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PACE Report No. 88-2

THE BEHAVIOUR OF SOLUBLE PETROLEUM PRODUCT DERIVED HYDROCARBONS IN GROUNDWATER PHASE III

"Working for a Better Environment"

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THE BEHAVIOUR OF SOLUBLE PETROLEUM PRODUCT DERIVED HYDROCARBONS IN GROUNDWATER

PHASE III

PACE REPORT NO. 88-2

Prepared for

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NOTICE

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ABSTRACT

This study contributes to the understanding of the processes controlling the migration or transport in groundwater, of selected organic compounds that dissolve in groundwater from petroleum products. Of particular concern are the monoaromatic hydrocarbons: benzene, toluene, and xylene isomers (BTX).

The approach has been to inject both BTX-spiked and gasoline-contacted groundwater into a shallow, sand aquifer and to monitor the migration and persistence of these contaminants as they move in response to groundwater flow. BTX concentrations were reduced from 1740 ug/L to less than 2 ug/L within 434 days by biodegradation and dispersive processes. Biodegradation was shown to continue to reduce BTX concentrations below 1 ug/L by utilizing oxygen available within the groundwater. Biodegradation of BTX was limited by the availability of oxygen. Laboratory investigations indicate denitrifying bacteria can reduce nitrate to nitrogen gas while transforming BTX in oxygen-limited environments. Nitrate addition to existing gasoline-contaminated groundwater was evaluated as a remediation technique by comparing the BTX mass and displacement of centre of mass for the nitrate-remediated and similar unremediated dissolved gasoline plumes. Nitrate addition enhanced the removal of toluene and m-xylene somewhat but most of the BTEX was removed aerobically prior to the complete overlap of the nitrate and BTEX plumes.

A three-dimensional numerical model, simulating the transport and biodegradative interaction of oxygen and BTX in groundwater, was used to examine the relative importance of site-specific, hydrogeological and biogeochemical parameters in controlling the persistence and mobility of BTX. Through a model sensitivity study, the results of the field research were generalized so to be applicable to other sites of interest. The initial BTX and dissolved oxygen concentrations, groundwater velocity, retardation factors and heterogeneity of the porous media had the most control on the rate of mass loss.

ABREGE

Cette étude a pour objet de contribuer à une meilleure compréhension des processus qui contrôlent la migration ou le transport dans les eaux souterraines de certains composés organiques provenant de produits pétroliers qui se dissolvent dans l'eau souterraine. Les hydrocarbures monoaromatiques, c'est-à-dire le benzène, le toluène et les isomères du xylène (BTX) revêtent un intérêt particulier.

L'approche utilisée a consisté à injecter de l'eau souterraine additionnée de BTX et contaminée d'essence dans une couche de sable aquifère à faible profondeur et à surveiller la migration et la persistance de ces contaminants lors de leur déplacement sous l'effet de l'écoulement des eaux souterraines. Les concentrations de BTX ont diminué de 1 740 µg/l à moins de 2 µg/l sur une période de 434 jours grâce aux processus de biodégradation et de dispersion. On a démontré que la biodégradation continue à réduire les concentrations de BTX à des niveaux inférieurs à 1 µg/l en utilisant l'oxygène disponible dans l'eau souterraine. La biodégradation des BTX était limitée par la quantité d'oxygène disponible. Selon des études en laboratoires, les bactéries dénitrifiantes peuvent décomposer les nitrates en gaz azote au cours de la transformation des BTX dans des milieux à faible concentration d'oxygène. On a évalué l'addition du nitrate à l'eau souterraine déjà contaminée par l'essence comme méthode de redressement en comparant la masse de BTX et le déplacement du centre de la masse des colonnes d'essence dissoute traitées au nitrate avec des colonnes semblables d'essence non traitées. L'addition du nitrate a amélioré dans une certaine mesure la réduction du toluène et du m-xylène mais la majeure partie des BTEX a été éliminée par action aérobie avant que les colonnes de nitrate et de BTEX se rejoignent.

Une modèle numérique en trois dimensions du transport et de l'interaction biodégradante de l'oxygène et des BTX dans l'eau souterraine a été utilisé pour examiner l'importance relative des paramètres hydrogéologiques et biogéochimiques spécifiques aux sites relativement à la persistance et la mobilité des BTX. On a généralisé les résultats des recherches menées sur le terrain au moyen d'un modèle de sensibilité afin qu'ils soient applicables à d'autres sites d'intérêt. Les concentrations initiales de BTX et d'oxygène dissout, la vitesse de l'eau souterraine, les facteurs de ralentissement et l'hétérogénéité du milieu poreux étaient les plus importants des facteurs déterminant le taux de diminution de la masse.

EXECUTIVE SUMMARY

Introduction

Following a spill of petroleum products on or below ground surface, the petroleum product infiltrates the vadose zone, moving down towards the water table. As the petroleum product migrates downwards, an immiscible residue is left behind. Depending upon the extent of the spill, petroleum in the subsurface may be limited to the residual phase in the vadose zone or it may also form a pool of free product which floats on top of the saturated zone. Both the residue and the free product may act as sources for the solubilization of petroleum constituents into the groundwater. Associated groundwater may be contaminated at levels above drinking water standards. The goal of this three phase research program, initiated in 1984, was to develop an improved understanding of the processes controlling the migration of selected organic compounds that dissolve in groundwater from petroleum products. Of particular concern are the monoaromatic hydrocarbons: benzene, toluene, and xylene isomers (termed BTX).

The specific objectives of this three-phase research program were: 1) to critically evaluate small-scale methods for measuring the retardation via sorption of BTX during movement in groundwater, 2) to determine the effects of both retardation by sorption and biodegradation on the migration of BTX in groundwaters, and 3) to assess the potential for biochemical remediation or clean-up of groundwaters contaminated by BTX. The first specific objective is dealt within the PACE Report 87-3. Most of the research for the second objective is discussed in the Phase I and Phase II reports (PACE Reports 85-3 and 86-1). This report and the PACE Report 87-3 describe the progress and conclusions of the third phase of this program during 1986 and 1987.

The specific objectives for Phase III were:

1. to evaluate and recommend the appropriate small-scale methods for measuring or assessing sorptive retardation of dissolved BTX as they migrate in groundwater

2. to complete long term monitoring of the Phase II BTX plume to determine the persistence of benzene, toluene and xylenes at low concentrations

3. to evaluate the migration of BTX when the complex spectrum of other water-soluble gasoline components is present and to compare this with the migration when these other organics are not present

4. to evaluate the addition of nitrate as a method for in situ clean-up or remediation of groundwater contaminated with gasoline-derived BTX

The first specific objective is dealt with in the PACE Report 87-3 while the other objectives are addressed in this report.

The approach of the three phase study has been to inject both BTX-spiked and gasoline-contacted groundwater into a shallow sand aquifer and to monitor the migration and persistence of these contaminants as they move in response to the natural groundwater flow. Auxillary laboratory experiments have also been conducted to elucidate the processes, such as sorptive retardation and biodegradation, which control the organic contaminants' mobility and persistence. Two major field injection experiments have been conducted. The first involved the injection of water spiked with specific contaminants and a non reactive tracer, namely benzene, toluene, p-, m-, and o-xylenes (BTX) and chloride. The second was a dual injection of water, part of which had contacted unleaded gasoline and so contained the water-soluble components benzene, toluene, ethyl benzene and xylenes (termed BTEX). A later injection behind this dual injection introduced nitrate into the groundwater upgradient from one of the BTEX-containing water volumes. During groundwater migration, the more mobile nitrate overtook the slightly retarded BTEX and the impact of this nitrate upon BTEX biodegradation was evaluated. All of these experiments were conducted in the shallow, unconfined, sand aquifer at Canada Forces Base Borden, Ontario.

Phase III results are described in the following sections.

The Persistence of BTX

The first injection experiment began in August 1984 and established that BTX was attenuated in the presence of oxygen to concentrations below 1 to 2 ug/L within about 434 days (PACE 86-1). Additional monitoring of groundwaters was undertaken to establish how low the concentrations of the BTX components had become in late 1985 and in 1986.

The additional groundwater sampling and analysis required the development of improved sampling protocols and analytical techniques with better sensitivity for BTX. Even then, considerable difficulty was encountered in collecting and analyzing groundwaters where BTX concentrations from 0.1 to 1 ug/L were of interest.

Only very low concentrations of BTX (<0.1 ug/L for each component) were found to have persisted for 750 days since the injection. BTX removal is mainly attributed to biodegradation by natural microbes present in the aquifer and active under aerobic (oxygen present) conditions. In addition, dispersion lowered BTX concentrations. These two processes - biodegradation and dispersion - produced the attenuation of BTX to concentrations of less than 0.1 ug/L.

The Nitrate Remediation Experiments

Laboratory studies indicated that denitrifying bacteria could biodegrade BTX in the absence of oxygen. These bacteria reduce nitrate (NO_3) to nitrogen gas (N_2) and oxidize organics, apparently including BTX. It appeared that the addition of nitrate could induce denitrifying bacteria to continue the biodegradation of BTX or BTEX when the available oxygen was consumed. This could decrease the persistence of BTEX in oxygen deficient, gasoline-contaminated groundwater and so could be a useful procedure for restoring water quality in such groundwater.

Two distinct volumes (2500 L each) of BTEX-containing groundwaters were established in the Borden aquifer by injecting groundwater, which had contacted gasoline, below the water table. The total BTEX concentration was about 880 ug/L. Four days after this injection, additional groundwater was injected 1.5 m upgradient of these two volumes. Behind one BTEX-mass, this injected water contained about 45 mg/L nitrate and 2000 mg/L chloride tracer. Behind the other, only unamended groundwater was injected. As these injected masses migrated with the groundwater flow, the BTEX components of one mass, slightly retarded due to sorption onto aquifer material, were overtaken by the non-sorbing chloride and nitrate. The other BTEX mass migrated without the presence of nitrate. Detailed groundwater sampling and analyses were conducted for 148 days and less extensive monitoring was conducted up to 365 days after injection. The data management and interpretation was similar to that described in PACE Report 86-1.

The impact of other gasoline-derived organics on the mobility and persistence of BTEX was assessed by comparing the results obtained for the 'unremediated' BTEX-containing mass with those obtained from the 1984 injection of BTX compounds only. The mobility of BTEX was unaffected as sorptive retardation was similar. BTEX and BTX mass removal rates were also very similar. In laboratory experiments, the presence of other organics had a significant impact in increasing the persistence of BTEX. The difference in laboratory and field removal rates was attributed to the physical and chemical processes occurring during solute transport which assisted in the removal of other organics dissolved from gasoline.

Nitrate addition, as an in situ remedial measure for gasoline-contaminated groundwater, was evaluated through comparison of the masses of BTEX remaining in groundwater and the postion of centres of mass of BTEX and nitrate in the unremediated and nitrate-remediated plumes. Some enhancement of BTEX mass removal rates in the presence of nitrate was interpreted from the field experiment. However, oxygen did not appear to become sufficiently limiting to adequately evaluate the potential of denitrifyers to produce enhanced biodegradation of BTEX in oxygen-free gasoline-impacted groundwaters. The field experiment did demonstrate, however, that a remedial solution containing nitrate could be injected into a gasoline-contaminated aquifer and the natural migration processes would mix the nitrate with BTEX without hydraulic controls, such as pumping, being required.

BTX Behaviour in Other Hydrogeologic Settings

The results of the Phases II and III research studies were applied to the prediction of the mobility and persistence of BTEX in other hydrogeologic settings. The organic solute transport model of MacQuarrie et al. (in submission) was used to examine the migration of dissolved hydrocarbons in shallow groundwaters. A model sensitivity analysis was used to define the hydrogeologic parameters most important to define during site investigations in order to estimate the likely behaviour of BTEX.

The modelling study indicated that, in uniform groundwater flow, a plume originating from a high concentration source will experience more spreading and relatively slower mass loss than a lower initial concentration plume because dissolved oxygen is quickly depleted in the former. It also showed that low dissolved oxygen concentrations cause slower organic mass loss, while the initial size of the microbial population has little effect. High groundwater velocities increase the rate of organic mass loss because of increased dispersion. However, the organic could still be found at unacceptable concentrations further from the source when compared to slow velocity settings because of increased advection. Sorbed organics were assumed unavailable for biodegradation, therefore increasing the retardation factor of an organic (transport in a soil with higher organic matter, for example) causes slower mass loss. The higher retardation would also limit the extent and migration rate of the dissolved hydrocarbons. For easily biodegraded organics, such as BTX, the kinetic parameters of biodegradation do not influence mass loss because the mixing of the organic and dissolved oxygen controls the biodegradation. This implies that, for these types of compounds, the kinetic biodegradation parameters do not need to be known with precision.

The model was used to predict migration in other hydrogeologic regimes. It showed that, in complex-structured heterogeneous media with complex flow fields, the bulk velocity, position and rate of spreading of an organic plume is strongly dependent on local-scale hydrogeological parameters. It is suggested that average transport parameters such as macrodispersivity may not be applicable to organic plume transport. Reliable predictions of the fate of organics in groundwater may require extensive knowledge of the distribution of hydrogeological properties of the aquifer.

Summary Report

To complete and bring together the three phases of research, two comunications will be prepared in 1988:

1. a summary report
2. a VCR presentation

The summary report will review all three phases and place the research findings into a practical context more appropriate for implementation by the oil industry. The results will be generalized so that they may be applied where gasoline contamination of groundwater occurs in hydrogeological settings other than permeable sand aquifers. Appropriate approaches and cautions concerning these findings will be included.

The VCR presentation will assist PACE and its members to visually understand the nature of this research and to utilize the results in their response to groundwater contamination events. It will also be a useful training tool for universities and professionals in the groundwater consulting industry.

SOMMAIRE

Introduction

A la suite d'un déversement de produits pétroliers à ou dessous la surface du sol, le produit pétrolier s'infiltre dans la zone vadeuse et se déplace en descendant vers la nappe phréatique. En se déplaçant vers le bas, le produit pétrolier laisse derrière un résidu non miscible. Selon l'importance du déversement, le pétrole dans le sous-sol peut être limité à une phase résiduelle dans la zone vadeuse ou il peut aussi former un dépôt de produit libre flottant au-dessus de la zone de saturation. Le résidu et le produit libre peuvent agir comme sources de solubilisation des constituants pétroliers dans l'eau souterraine. Les eaux souterraines affectées peuvent être contaminées à des niveaux supérieurs aux normes d'eau potable. L'object de ce programme de recherches en trois phases, amorcé en 1984, est de favoriser une meilleure compréhension des processus contrôlant la migration de certains composés organiques qui se dissolvent de produits pétroliers dans les eaux souterraines. Les hydrocarbures monoaromatiques, c'est-à-dire le benzène, le toluène et les isomères du xylène (désignés BTX) revêtent un intérêt particulier.

Les objectifs précis de ce programme de recherches en trois phases étaient: 1) effectuer une évaluation critique des méthodes à petite échelle destinées à la mesure des facteurs de ralentissement par sorption des BTX lors de leur déplacement dans les eaux souterraines; 2) déterminer les effects du ralentissement par sorption et de la biodégradation sur la migration des BTX dans les eaux souterraines, et 3) évaluer les possibilités de redressement ou d'épuration biochimiques des eaux souterraines contaminées par les BTX. On traite du premier de ces objectifs précis dans le rapport de l'APCE no. 87-3. La majeure partie des recherches apparentées au deuxième objectif est exposée dans les rapports sur les Phases I et II (rapports de l'APCE no. 85-3 et 86-1). Le présent rapport et le rapport de l'APCE no. 87-3 décrivent l'évolution de la troisième phase pendant la période 1986 et 1987 et les conclusions qu'on en a tirées.

Les objectifs précis de la Phase III étaient les suivants:

1. évaluer et recommander des méthodes à petite échelle pour mesurer ou évaluer le ralentissement par sorption des BTX dissouts lors de leur migration dans les eaux souterraines;

2. achever la surveillance à long terme de la colonne de BTX de Phase II dans le but de déterminer la persistance du benzène, du toluène et des xylènes à de faibles concentrations;

3. évaluer la migration des BTX lorsque l'éventail complexe des autres composantes hydrosolubles de l'essence est présent et en faire une comparaison avec la migration lorsque ces autres matières organiques ne sont pas présentes;

4. évaluer l'addition du nitrate à titre de méthode d'épuration ou de redressement in situ des eaux souterraines contaminées par des BTX dérivés de l'essence.

Le rapport de l'APCE no. 87-3 traite du premier de ces objectifs précis. Les trois autres font l'objet du présent rapport.

L'approche utilisée dans le cadre de cette étude en trois phases a consisté à injecter de l'eau souterraine additionnée de BTX et contaminée d'essence dans une couche de sable aquifère à faible profondeur et de surveiller les migrations et la persistance de ces contaminants lors de leur déplacement sous l'effet de l'écoulement naturel des eaux souterraines. On a également mené des expériences supplémentaires en laboratoire afin d'élucider les processus, tel le ralentissement par sorption et la biodégradation qui déterminent la mobilité et la persistance des contaminants organiques. Deux expériences majeures d'injection ont été effectuées sur le terrain. La première a consisté à injecter de l'eau additionnée de contaminants précis et d'un traceur non réactif, soit le benzène, le toluène, le p-xylène, le m-xylène et le o-xylène (BTX) et des chlorures. La deuxième expérience a consisté en une double injection d'eau dont une partie était contaminée par de l'essence sans plomb et contenait alors les composantes hydrosolubles, le benzène, le toluène, l'éthylbenzène et les xylènes (désignés BTEX). Une deuxième injection à la suite de cette double injection a introduit du nitrate dans l'eau souterraine en amont d'une des colonnes d'eau contenant les BTEX. Au cours de la migration de l'eau souterraine, le nitrate a rattrapé le BTEX légèrement ralenti et on a évalué l'effet que ce nitrate a eu sur la biodégradation. Toutes ces expériences ont été menées dans la couche de sable aquifère non confinée à la Base des Forces canadiennes de Borden (Ontario).

Les résultats de la Phase III de l'étude sont résumés dans les sections suivantes.

La persistance des BTX

La première expérience d'injection a débuté en août 1984 et a établi que la teneur en BTX diminuait en présence de concentrations d'oxygène inférieures à de 1 à 2 µg/l dans une période d'environ 434 jours (APCE 86-1). On a fait un suivi supplémentaire des eaux souterraines afin de déterminer jusqu'à quel point les concentrations de composantes BTX avaient diminué à compter de la fin de 1985 et en 1986.

L'échantillonnage et l'analyse supplémentaires des eaux souterraines ont nécessité l'élaboration de protocoles d'échantillonnage améliorés et de méthodes d'analyse beaucoup plus sensibles aux BTX. Malgré cela, on a éprouvé beaucoup de difficulté en ce qui a trait au prélèvement et à l'analyse des eaux souterraines là où il s'agissait de concentrations de BTX variant de 0,1 à 1 µg/l.

On a constaté que seulement de très faibles concentrations de BTX (0,1 µg/l de chaque composante) avaient persisté pour 750 jours suivant l'injection. L'élimination des BTX est attribuée surtout à la biodégradation opérée par les microbes qui sont naturellement présents dans l'aquifère et actifs dans des conditions aérobies (en présence d'oxygène). En plus, la dispersion a diminué les concentrations de BTX. Ces deux processus - la biodégradation et la dispersion - ont entraîné une diminution des concentrations de BTX à des niveaux inférieurs à 0,1 µg/l.

Les expériences de redressement au nitrate

Selon des études en laboratoire, les bactéries dénitrifiantes peuvent décomposer les BTX en l'absence d'oxygène. Ces bactéries réduisent le nitrate (NO3) en gaz azote (N2) et oxydent les composés organiques y compris, semble-t-il, les BTX. Il parraissait que l'addition du nitrate pourrait amener les bactéries dénitrifiantes à continuer la biodégradation des BTX ou des BTEX après que l'oxygène disponible avait été consommée. Cela pouvait réduire la persistance des BTEX dans les eaux souterraines à teneur insuffisante en oxygène contaminées par l'essence et s'avérer donc une procédure utile pour le rétablissement de la qualité des eaux souterraines dans de telles circonstances.

Deux volumes distincts (2 500 l chacun) d'eau souterraine contenant des BTEX ont été établis dans l'aquifère de Borden en injectant de l'eau souterraine, qui avait été contaminée par de l'essence, dessous la nappe phréatique. La concentration globale de BTEX s'élevait à environ 880 µg/l. Quatre jours après cette injection, on a injecté de l'eau souterraine à une distance de 1,5 m en amont de ces deux volumes. L'eau injectée derrière l'une des masses de BTEX contenait environ 45 mg/l de nitrate et 2 000 mg/l de traceur sous forme de chlorure. L'eau injectée derrière la deuxième masse ne contenait aucun amendement. A mesure que ces masses migraient sous l'effet de l'écoulement de l'eau souterraine, les composantes BTEX d'une des masses, légèrement ralenties par la sorption sur la matière aquifère, étaient rattrapées par le nitrate et le chlorure non sorptifs. La deuxième masse de BTEX migrait sans qu'il y ait de nitrate présent. Des échantillonnages et des analyses détaillés des eaux souterraines ont été effectués sur une période de 148 jours et une surveillance moins intensive s'est poursuit pour 365 jours suivant l'injection. La gestion et l'interprétation des données se sont déroulées d'une manière semblable à celle décrite dans le rapport de l'APCE no. 86-1.

On a évalué l'effet des autres dérivés organiques de l'essence sur la mobilité et la persistance des BTEX en comparant les résultats obtenus d'une masse contenant des BTEX n'ayant pas fait l'objet de redressement avec les résultats obtenus en 1984 de l'injection ne contenant que des composés BTX. La mobilité des BTEX n'a pas été affectée parce que les taux de ralentissement par sorption etaient semblables. Les taux d'élimination des masses de BTEX et de BTX étaient également très rapprochés. Selon les expériences en laboratoire, la présence des autres composés organiques avait un effect significatif en ce qui a trait à l'augmentation de la persistance des BTEX. La différence entre les taux d'élimination observés sur le terrain et dans le laboratoire est attribuable aux processus physiques et chimiques qui s'opèrent au cours du transport des solutés qui ont contribué à l'élimination des autres matières organiques dissoutes de l'essence.

On a évalué l'addition du nitrate, à titre de mesure de redressement in situ des eaux souterraines contaminées par l'essence, en comparant les masses de BTEX demeurant dans l'eau souterraine et la position des centres des masses de BTEX et de nitrate des colonnes non traitées et des colonnes traitées au nitrate. L'expérience sur le terrain a indiqué une certaine augmentation des taux d'élimination de la masse de BTEX. Cependant, la teneur en oxygène n'a pas semblé tomber suffisamment pour permettre une évaluation satisfaisante du potentiel que possède les bactéries dénitrifiantes pour l'amélioration de la biodégradation des BTEX dans les eaux souterraines à faible teneur en oxygène contaminées par l'essence. L'expérience sur le terrain a démontré cependant qu'on peut injecter une solution de redressement contenant du nitrate dans un aquirère contaminé par l'essence et que les processus naturels de migration mélangeraient le nitrate et les BTEX sans nécessiter de contrôle hydraulique tel le pompage.

Le comportement des BTX dans d'autres milieux hydrogéologiques

Les résultats des Phases II et III du programme de recherches ont été utilisés pour prédire la mobilité et la persistance des BTEX dans d'autres milieux hydrogéologiques. On a utilisé le modèle de transport des solutés organiques de MacQuarrie et al. (en voie de soumission) pour examiner la migration des hydrocarbures dissouts dans les eaux souterraines à faible profondeur. On a utilisé un modèle d'analyse de sensibilité pour définir les paramètres hydrogéologiques qui seraient les plus importants à définir aux fins d'estimation du comportement probable des BTEX lor des examens des sites.

L'étude de modélisation a démontré que, dans des conditions d'écoulement uniforme des eaux souterraines, une colonne provenant d'une source à forte concentration occasionnera plus de dispersion et une diminution relativement moins prononcée de masse qu'une colonne dont l'origine est une source à concentration moindre, du fait que l'oxygène est rapidement épuisé dans le premier cas. L'étude a également démontré que les faibles concentrations d'oxygène dissout occasionnent des pertes de masse organique moins rapide tandis que la taille initiale de la population microbienne n'a que très peu d'effet. Les hautes vitesses d'eau souterraines augmentent le taux d'élimination de la masse organique à cause de la dispersion accrue. Cependant, on pouvait détecter des concentrations inacceptables de composés organiques à des distances plus éloignées de la source comparativement au cas de vitesses moindres en raison de l'advection accrue. Les matières organiques sorbées étaient présumées non disponibles aux fins de biodégradation. Par conséquent, l'augmentation du facteur de ralentissement d'un composé organique (le transport dans un sol avec une plus forte teneur organique, par exemple) ralentit le rythme d'élimination de la masse. Le ralentissement plus élevé pourrait également limiter l'étendue et le rythme de migration des hydrocarbures dissouts. Pour ce qui est des composés organiques facilement biodégradables, les paramètres cinétiques de biodégradation n'ont aucune influence sur la perte de masse parce que le mélange des composés organiques et de l'oxygène dissout contrôle la biodégradation. Cela implique qu'il n'est pas nécessaire, en ce qui concerne ce genre de composés, de connaître avec précision les paramètres cinétiques de biodégradation.

On a utilisé le modèle pour prédire la migration dans d'autres milieux hydrogéologiques. Le modèle a montré que, dans les cas de milieux hétérogènes à structure complexe avec des champs d'écoulement complexes, la vitesse de la masse et la position et le taux de dispersion d'une colonne organique sont fortement influencés par les paramètres hydrogéologiques à échelle locale. Les résultats portent à croire que les paramètres moyens de transports tels la "macrodispersibilité" pourraient ne pas s'appliquer au transport des colonnes de composés organiques. Pour faire des prévisions fiables du devenir des composés organiques dans les eaux souterraines, nous aurions probablement besoin de connaissances beaucoup plus approfondies de la distribution des propriétés hydrogéologiques de l'aquifère en question.

Rapport sommaire

Deux communications seront produites en 1988 pour compléter et rattacher ensemble les trois phases du programme de recherches. Ce sont:

1. un rapport sommaire; et
2. une présentation vidéo

Le rapport sommaire passera en revue les trois phases du programme et situera les constatations des recherches dans un contexte pratique qui convient mieux à la mise en application par l'industrie pétrolière. Les résultats seront généralisés de facon à ce qu'on puisse les appliquer à des cas de contamination d'eaux souterraines par l'essence dans des milieux hydrogéologiques autres que les couches perméables de sable aquifères. Les approches appropriées et les précautions à prendre lors de l'application de ces constatations y seront incluses.

La présentation vidéo aidera l'APCE et ses membres à saisir visuellement la nature de ces recherches et d'en utiliser les résultats dans le cadre de leurs réponses aux occurrences de contamination des eaux souterraines. Cette présentation servira également d'outil de formation destiné aux universités ainsi qu'aux professionnels dans l'industrie de conseils en matière d'eaux souterraines.

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Chapter I

GOALS AND OBJECTIVES

The goal of this three-phase research program, initiated in 1984, was to develop an improved understanding of the processes controlling the migration or transport in groundwater, of selected organic compounds that dissolve in groundwater from petroleum products. The specific objectives of this program were five-fold:

1. To assess the accuracy and applicability of the conventional methods, and two newly developed methods, for determining the retardation by sorption onto aquifer materials of the selected organic compounds, during transport by groundwater in sand aquifers.

2. To develop and assess *practical methods* for determining the extent to which biodegradation will remove the selected organic compounds during migration in sand aquifers.

3. To test and evaluate the balanced nutrient method of stimulating biodegradation as a remedial action for groundwater zones contaminated with the selected organic compounds and to evaluate the role of dispersion in this method.

4. To make use of the information obtained in the three objectives mentioned above in evaluating other options for remedial action that have been described in the literature or are currently being developed.

5. To broaden the results of this study to consider migration and possible remedial actions pertinent to other hydrogeological environments.

This research will aid the petroleum industry and its consultants in the design and use of groundwater monitoring networks, in the assessment of both the rate of migration and the fate of dissolved organic components and in the evaluation of options for remedial measures required to limit or reduce the extent of such contaminants. Specific benefits will include:

1. evaluation of the natural processes that control contaminant movement

2. evaluation of means to assess sorption and biodegradation processes that could slow down and limit the movement of contaminants

3. provision of a scientifically-evaluated in situ tester for field measurement of sorption

4. evaluation of in situ remedial techniques using microbial degradation

5. identification of hydrogeologic parameters critical to properly deal with groundwater contamination by BTX (benzene, toluene, xylenes).

Specific tasks undertaken in Phase I were:

1. the performance of calculations, laboratory experiments and field experiments with an in situ tester to define the sorptive characteristics of the Borden sand for BTX

2. the design and implementation of a natural gradient injection test at the Borden site to evaluate the rate of movement and the fate of BTX dissolved in groundwater. The results were also used to assess the suitability of laboratory tests as predictive tools

3. the critical comparison of the various laboratory and field methods for assessing the slowing down or retardation of BTX in groundwater.

In Phase II, some of these tasks continued and additional tasks were undertaken. The specific Phase II tasks were:

1. to complete the natural gradient injection experiment at the Borden site in order to evaluate the migration of BTX through the aquifer and to compare laboratory estimates of sorptive retardation and biodegradation rates with the observations from the field experiment

2. to assess the ability of the microbial population at the field site to degrade BTX under various environmental conditions and at various initial concentrations and to determine the most significant degradation pathways and degradation products

3. to assess various nutrient additions designed to enhance biodegradation

4. to obtain a more substantial basis for identifying the advantages and limitations of the various procedures to determine sorptive retardation of BTX. This involves comparing the results of calculations and laboratory tests for BTX sorption using additional sandy materials having a range in organic carbon content in order to recommend procedures for a variety of hydrogeologic regimes.

The specific objectives for Phase III were:

1. to evaluate and recommend the appropriate small-scale methods for measuring or assessing sorptive retardation of dissolved benzene, toluene and xylenes (termed BTX) as they migrate in groundwater

2. to evaluate the migration of BTX when the complex spectrum of other water-soluble gasoline components is present and to compare this with the migration when these other organics are not present.

3. to evaluate the addition of nitrate as a method for in situ clean-up or remediation of groundwater contaminated with gasoline-derived BTX.

4. to evaluate the hydrogeologic parameters most important in controlling the mobilitiy, fate, and persistence of BTX in other hydrogeologic regimes

This research commenced in April, 1984 and the progress in Phase I until the end of 1984 is summarized in PACE Report No. 85-3 (Patrick et al., 1985). The Phase I report presented the laboratory and field study of the sorptive characteristics of the Borden sand with respect to BTX as well as the design and initial results of the natural gradient injection experiment conducted within the Borden sand. The Phase II report (PACE Report 86-1) emphasized the results of this natural gradient injection experiment and the related laboratory tests of retardation and biodegradation. Other aspects also included in Phase II research were the expanded sorption testing utilizing additional sandy materials and the microbial testing of potential remedial measures employing enhanced biodegradation methods. The first specific objective of Phase III is addressed in PACE Report 87-3. This report presents the laboratory, field and modelling studies undertaken for the remaining specific objectives of Phase III.

Chapter II

THE BTX INJECTION EXPERIMENT, 1984 TO 1986

2.1 INTRODUCTION

On August 9 and 10, 1984, 1800 litres of groundwater spiked with dissolved constituents (Table 2.1) was injected into the unconfined sand aquifer at Canada Forces Base Borden, near Barrie, Ontario. This formed a relatively uniform, spherical plume below the water table. The essentially horizontal groundwater flow caused the benzene, toluene, xylenes and chloride constituents to move horizontally. The injection procedure and the results of monitoring the movement and persistence of these constituents for 434 days are presented by Patrick et al. (1985 and 1986).

Table 2.1: Amounts of Chemicals Injected

Chemical	Estimated Mass	Average Injection Concentration
Benzene	4.25 g*	2360 ug/L
Toluene	3.16 g	1750 ug/L
o-Xylene	231 g	1280 ug/L
p-Xylene	1.94 g	1080 ug/L
m-Xylene	1.96 g	1090 ug/L
Chloride	2.30 kg as Cl^-	1280 mg/L

* actual benzene values may be slightly lower due to contamination by hypovial septa. (Patrick, 1986)

2.2 THE MONITORING NETWORK

A network sufficient to monitor the migration of the injected contaminants for about 265 days had been installed in 1984 as part of the PACE-sponsored research. Additional multilevel sampling piezometers were constructed and installed in 1985 and 1986 with API support to provide monitoring of the plumes up to about 775 days following injection. All of the additional piezometers were 14 point, teflon tubing type (Patrick et al., 1985).

The location of the monitoring network is shown in Figure 2.1. The piezometers installed in August, 1985 (x coordinates of rows: 28 m to 34 m) were closely spaced to detect small anaerobic zones where BTX might persist. More uncertainty existed as to the direction of migration, so piezometers were installed over a considerable distance across the estimated path of the contaminants. The additional piezometers were located (x coordinates of 44 and 52 m) to intercept the injected contaminants after 650 to 750 days of travel. The contaminant movements were predicted from the velocities determined by Patrick et al. (1986).

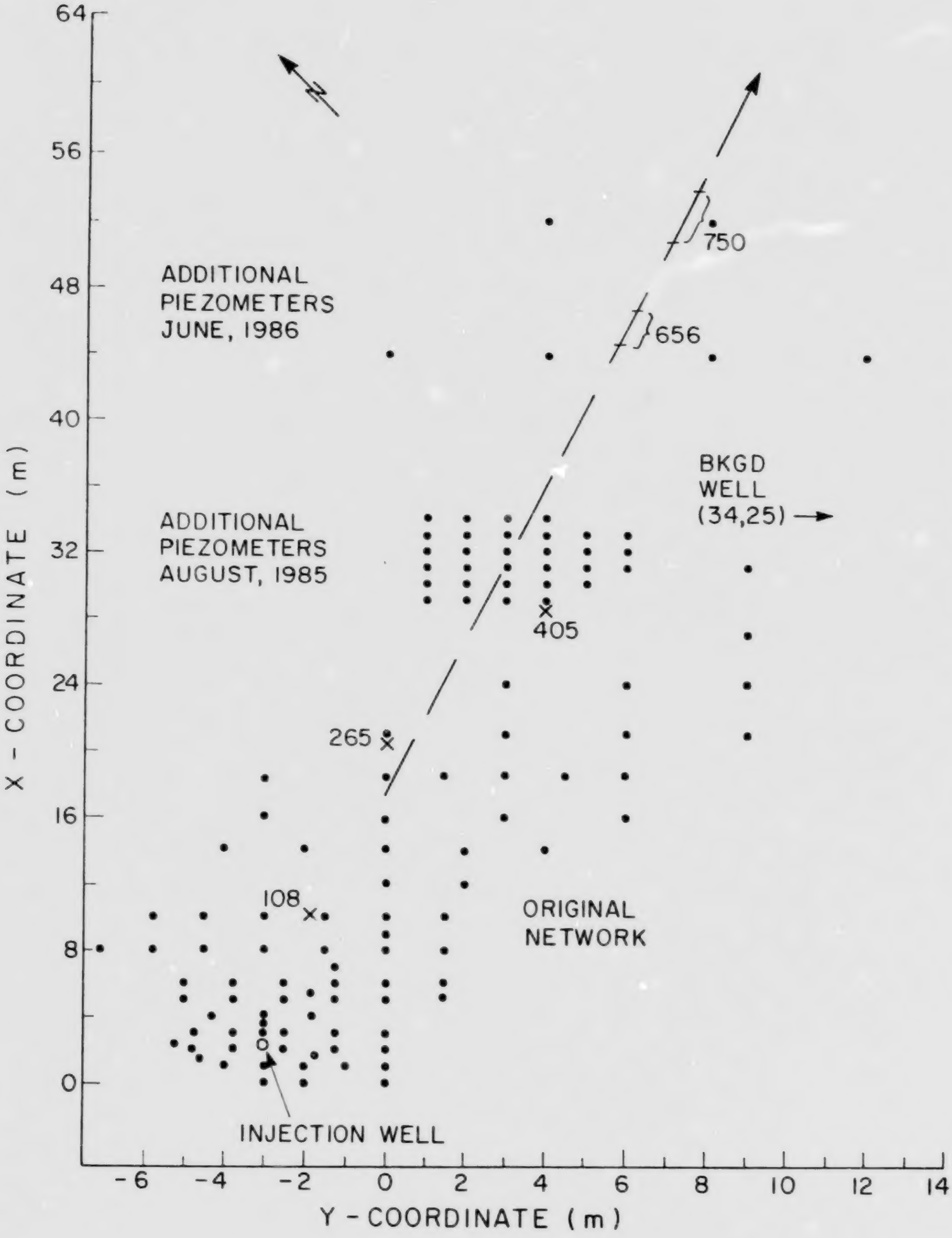
2.3 BTX BEHAVIOUR, 1984-1985

A horizontal two-dimensional illustration of the behaviour of the chloride, benzene, and toluene plumes during transport up to day 108 is presented in Figure 2.2 from Patrick et al. (1986). Shown are contours of the solute mass distribution at 3, 53, and 108 days after injection. The plots are constructed from vertically integrated concentration values, where each value represents the total mass of solute in the groundwater at that piezometer.

During migration, the chloride plume elongated only in the direction of groundwater flow, indicating significant longitudinal dispersion but little lateral dispersion. This behaviour is consistent with the results of previous tests of dispersion in the Borden study area (Mackay, 1986; Sudicky et al., 1983). The organic solutes did not elongate to the same extent as chloride, but rather shrank in size indicating a significant loss of dissolved mass. The size reduction is clearly evident for toluene, which shows no elongation through time.

The changes in total mass of the injected solutes over the initial 434 days of this experiment are shown in Figure 2.3 and are discussed by Patrick et al. (1985, 1986), Barker et al. (1987) and Patrick (1986). Snapshots of the BTX distributions up to 108 days revealed that BTX biodegraded rapidly when oxygen was present, but persisted where oxygen was absent. The small anaerobic zones within the aquifer were the sampling target for days 273 to 434. Results af these sampling sessions are listed in Table 2.2. The persistence of a small mass of benzene up to 434 days reflects the migration of residual benzene in thin, oxygen-free layers of the Borden sand aquifer. It is cautioned that Figure 2.3 does not show biodegradation rates for the monoaromatics, but shows the time required for sufficient oxygen to penetrate all of the BTX plumes to bring about their biotransformation.

Figure 2.1: The monitoring network, observed centres of benzene mass up to day 410 (x) and the ranges of predicted centres of benzene mass for days 656 and 750.



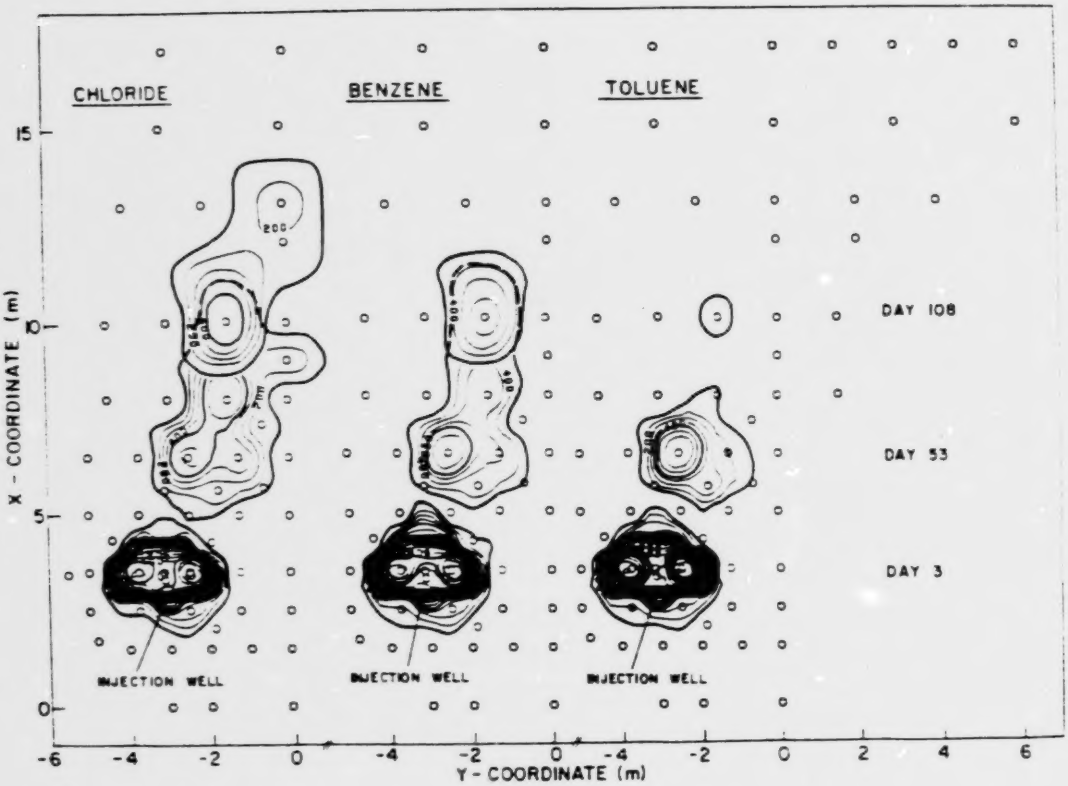


Figure 2.2: Contour plots of vertically integrated concentrations showing chloride, benzene and toluene plumes at 3, 53, and 108 days after injection. Units are mg.m. L^{-1}.

2.4 BTX BEHAVIOUR, 1986

2.4.1 Monitoring Concept

It is currently thought that there exists a finite substrate concentration below which bacterial utilization of an organic compound does not occur. This concentration is referred to as the threshold concentration for growth (Schmidt and Alexander, 1985) or S_{min} (Bouwer and McCarty, 1984). The concept of S_{min} or threshold is defined as the substrate concentration which limits bacterial growth. It has been suggested that threshold concentrations may be responsible for the persistence of trace levels of organic compounds in natural waters (Alexander, 1985). Organic compounds may exist at concentrations below their theoretical threshold. Utilization at concentrations below their theoretical threshold level may occur by cometabolism (Alexander, 1985) or secondary utilization (Bouwer and McCarty, 1984) if another substrate is present at concentrations high enough to support growth. Trace levels of organic compounds may also be utilized for cell maintainence if the bacterial population is not actively growing (Alexander, 1985).

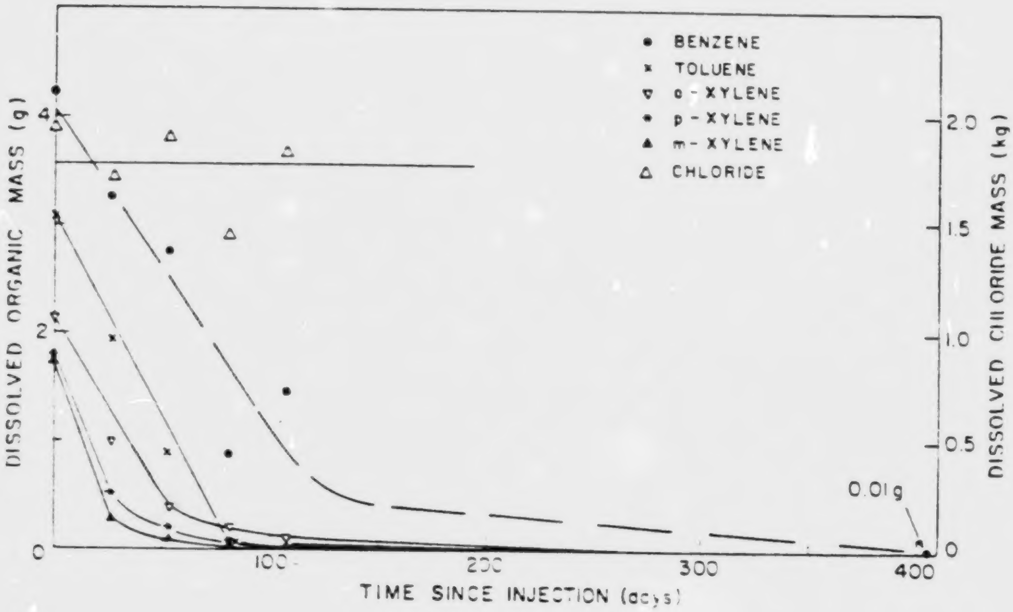


Figure 2.3: The calculated masses of BTX and chloride in the plume.

It was hypothesized that if significant concentrations of BTX (>1 ug/L) were to persist beyond day 434 (i.e.into 1986) they would only do so because the aerobic biotransformation process had a threshold concentration beyond which the microbes would not biotransform BTX. Dispersive mixing of threshold concentra-

Table 2.2: Summary of Plume Sampling - Days 273 to 434

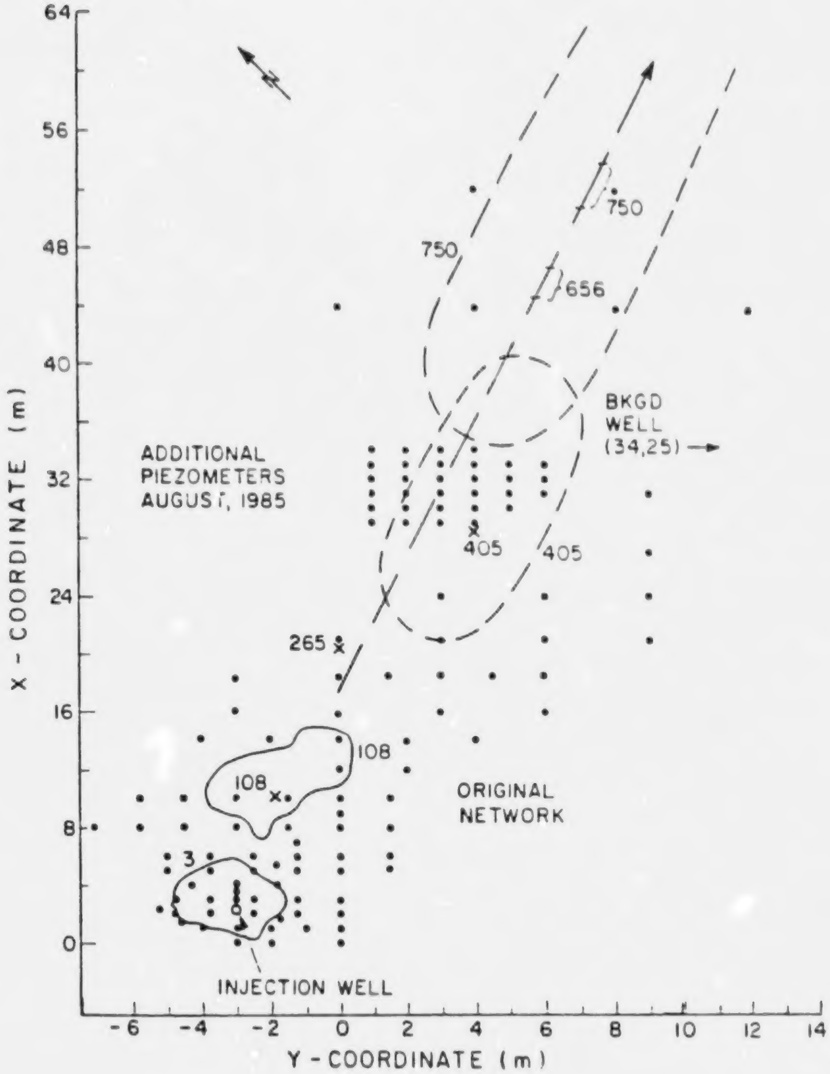
Sampling Date	Days Since Injection	Piezometers Sampled[1]	Results[2]
30/4/85	273	Rows 9 to 13 (16 to 24)	Benzene only in piezometer 11-0
8/5/85	280	Rows 8 to 12 (14 to 20)	Benzene only in point 10-0-10
23/5/85	295	Piezometer 11-0 (20)	no BTX
29/8/85	385	Rows 29 to 34 (29 to 34)	Cl only
9/9/85	396	" , right side	Benzene only in 7 points
18/9/85	405	"	No BTX found; analytical problems
26/9/85	413	", points 8-14	Benzene only in 3 points
3/10/85	420	"	Benzene only in 1 point
9/10/85	426	"	Benzene only in 1 point
16/10/85	434	"	no BTX found

1 - See Figure 2.1 for piezometer locations; brackets indicate x-coordinates of rows
2 - Data are listed in Appendix C

tions of BTX with uncontaminated groundwater would result in the occurrence of lower or "sub-threshold" (<1 ug/L) concentrations within the aquifer. BTX could also persist in anaerobic zones due to the very slow anaerobic biodegradation rates of BTX (Patrick et al., 1986). However, the process of dispersion within the aquifer seemed to re-oxygenate anaerobic zones. Thus, it was concluded that if BTX were to persist for more than 434 days, it would do so in either shrinking anaerobic zones or a sub-threshold concentrations (<1 to 2 ug/L) in widespread plumes. The small anaerobic zones were the major target for sampling in 1985. BTX did not seem to persist, so the sub-threshold or "residual" plumes became the target for sampling in 1986. The design of the monitoring network reflects these concepts of BTX persistence.

This sub-threshold BTX plume would expand with time due to dispersion during transport. The greatest expansion would be longitudinal to groundwater flow; transverse expansion, both lateral and vertical, is much less significant (Patrick et al., 1986; Freyberg, 1986; Sudicky, 1986). The expansion of this residual BTX plume was assumed to be the same as that observed for chloride in this experiment (Patrick et al., 1986) and in a previous experiment at this site (Mackay et al., 1986). The expected benzene plume boundaries on days 410, 656 and 750 are shown in Figure 2.4. This plume was the target of sampling during 1986. Definition of the residual masses of BTX for this plume would have required a very extensive sampling utilizing a larger piezometer network. Rather, fewer samples were collected and analyzed to establish whether such a residual plume persisted.

Figure 2.4: **The approximate outlines of the benzene plume on days 3, 108 and the expected outlines of a residual benzene plume on days 405 and 750.**


64
56
48
40
32
24
16
8
0
X - COORDINATE (m)
-6
-4
-2
0
2
4
6
8
10
12
14
Y - COORDINATE (m)
N
750
750
656
BKGD WELL (34,25)
ADDITIONAL PIEZOMETERS AUGUST, 1985
405
405
265
108
108
3
ORIGINAL NETWORK
INJECTION WELL

2.4.2 Sampling and Analyses

Prior to June 5, 1986 groundwater samples were collected using the sampling manifold discussed by Patrick et al. (1985,1986) and in Chapter III of this report. The BTX concentrations were determined using a microextraction gas chromatographic (GC) technique described in Appendix B. The method detection limits for each organic ranged from 0.4 ug/L to 1.4 ug/L.

Since most of the 1986 monitoring was attempting to find sub-threshold concentrations, perhaps at sub-ug/L levels, a more sensitive analytical technique was required. A purge-and-trap, gas chromatography/mass spectrometry (PT-GC/MS) procedure was developed (see Appendix B). This procedure has very low method detection limits of 10 to 62 ng/L ('ppt') (see Appendix B) but is much slower and much more susceptible to analytical problems and contamination during sampling.

The 14 point sampling manifold was used until July 9, 1986. At this time it was concluded that it could not be adequately flushed to prevent cross-contamination of samples. Subsequently, a 2 point sampling manifold of similar function was constructed and used. When a rigorous sampling and manifold flushing protocol was followed, this system was considered to introduce a negligible bias in the results. It was shown to be capable of producing negligible or not-measurable cross-contamination effects but the possible bias introduced by either sorption or volatilization of BTX at these sub-ug/L concentrations has not been evaluated. It is assumed that such bias is similar to that reported for the 14 point manifold at ug/L concentrations, i.e. -5% (Patrick et al., 1986).

This new sampling system and PT-GC/MS analysis was attempted on 4 occasions on July 9, 1986 and thereafter (see Table 2.3). On only one occasion, August 29, 1986 were reliable, sensitive results obtained. This attests, in part at least, to the difficulties with this sampling and analytical technique. It cannot be recommended for routine monitoring at this time. It may be useful in other research projects, if further evaluation confirms its reliability.

Table 2.3: Summary of Plume Sampling - Days 656 to 775

Sampling Date	Days Since Injection	Piezometers Sampled[1]	Results[2]
27/5/86	656	Row 44, points 9, 11,13,14 (44)	no BTX (< 1 to 2 ug/L)
5/6/86	665	"	results lost
11/6/86	671	"	BTX detected but probable contamination
9/7/86	699	Rows 44,52, points 4,6,8,10,12,14 (44,52)	"
24/7/86	714	"	"
29/8/86	750	"	BTX found at sub ug/L
23/9/86	775	Row 52, points 4,6,8,10,12 (52)	BTX detected but analytical contamination

1 - See Figure 2.1 for piezometer locations; brackets indicate x-coordinates of rows
2 - Data are listed in Appendix C

2.4.3 Results of the 1986 Plume Monitoring

The results from the June 11, 1986 sampling (day 671) are suspect because samples of organic-free distilled water (blanks) taken via the manifold occasionally contained similar levels of BTX as did groundwater samples. Blank-corrected BTX concentrations were calculated by subtracting the BTX concentrations of the blank taken immediately prior to the groundwater from the concentrations found in that groundwater. Detailed results are shown in Appendix C and summarized in Table 2.3. BTX concentrations ranged from the detection limits to about 350 ng/L (340 ng/L corrected), with toluene consistently being present at the highest concentrations.

The July 9, 1986 sampling did not find benzene or p-xylene but up to 700 ng/L toluene, 50 ng/L m-xylene and 20 ng/L o-xylene. Blanks contained no significant BTX, but were only taken after the groundwater sampling was completed. Therefore, they may not be representative.

The results from the July 24, 1986 sampling are also suspect. The manifold had been previously used in laboratory tests with solutions of high BTX concentration. The first piezometer to be sampled (44-12) had unreasonably high BTX concentrations (up to 2 ug /L of each). This is considered to represent carry-over from the previous laboratory waters. Other data are also suspect since blanks taken by sampling organic-free water between sampling piezometers contained up to 40 ng/L BTX. Also, the background well (34-25), a teflon multilevel well-removed from the BTX plume, produced water apparently containing 58 to 77 ng/L toluene, 12 to 45 ng/L m-xylene and 39 to 74 ng/L o-xylene and traces of benzene and p-xylene. These are similar to the levels encountered in the other piezometers. This illustrates the tremendous sampling problems associated with sub-ug/L detection. Apparently, exceptional cleaning of the sampling equipment is required if it is exposed to mg/L BTX concentrations.

The analyses from the sampling conducted on August 29, 1986 were the most reliable. Results are shown in Table 2.4 and in Appendix C. Organic-free water drawn through the sampling manifold in the field did not contain detectable BTX. Groundwater from the background piezometer (34-25) was also always free of detectable BTX. The points 4, 6, 8, 10 and 12 of piezometer 52-8 yielded groundwater containing only rare traces (< 15 ng/L) of BTX. Similar points of piezometer 52-4 yielded groundwaters containing low BTX concentrations, ranging up to 75 ng/L toluene from point 6. Only point 12 of piezometer 44,0 produced groundwater with a significant trace of toluene (11 ng/L). Other groundwaters from 44-0, 44-4, 44-8, and 44-12 were free of BTX.

The results from the August 29, 1986 sampling suggest that a BTX plume of very low concentrations still persisted 750 days after injection. Toluene and p- and o-xylene were the most commonly detected organics and were generally in the highest concentration. This was surprising, given the apparent persistence of ug/L concentrations of only benzene up to day 434.

The residual plume expansion due to dispersion should have brought about concentration reductions. It is assumed that the maximum BTX concentrations in the plume decreased in the proportion that the plumes expanded longitudinally. That is, if the benzene plume doubled in length, the maximum benzene concentration will have declined by a factor of 2 due to dispersion.

The residual, non-biotransformable BTX plumes were taken to initially occupy the volume of the injected groundwater as defined for day 3 (Figure 2.4). Although the measured BTX plumes shrank thereafter, the residual, non-biotransformable BTX plumes were hypothesized to have expanded as the chloride plume did. Up to day 273 (434 for benzene), the maximum BTX concentrations were controlled by the biotransformation of the high BTX concentrations. Beyond this day, the maximum BTX concentrations are assumed to have been controlled by dispersive dilution only - the residual BTX were non-biotransformable. Thus the maximum toluene or xylene concentrations at day 273 were assumed to be 2 ug/L and the maximum benzene concentration at day 434 was assumed to be 1 ug/L since these values are the approximate method detection limits for the GC analysis. The projected, maximum BTX concentrations were then predicted by the

Table 2.4: BTX Concentrations in Samples Collected 29/8/87 (day 750). Results are concentrations in ng/L.

Piezometer Point	Concentrations (ng/L) Benzene	Toluene	p-Xylene	m-Xylene	o-Xylene
34,25-6[1]	-	-	-	-	-
blank[2]	-	-	-	-	-
52,8-4	8*	15*	-	6*	-
-6	-	-	-	-	-
-8	-	-	11*	-	-
-10	-	-	-	-	-
-12	-	-	-	-	-
blank	-	-	-	-	-
52,4-4	-	-	58	-	-
-6	22*	75	20	15	40
-8	10*	52	7*	-	42
-10	-	33	6*	-	-
-12	4*	36	8*	1*	-
blank	-	-	-	-	-
34,25-6	-	-	-	-	-
44,0-12	-	11*	-	3*	-
-14	-	-	-	1*	-
44,4-12	-	-	-	-	-
-14	-	-	-	-	-
blank	-	-	-	-	-
44,8-12	-	-	-	-	-
-14	- --	-	-	-	
44,12-12	-	-	-	-	-
-14	-	-	-	-	-
blank	-	-	-	-	-
34,25-6	-	-	-	-	-
blank	-	-	-	-	-

- : not detected
* : below the method detection limit (MDL) shown in Appendix B.
1 : background groundwater
2 : organic free water sampled with the manifold

degree of expected plume expansions. Table 2.5 lists the expected plume expansions, based on the behaviour of chloride plumes (Freyberg, 1986), and the calculated maximum BTX concentrations.

Although the 1986 sampling was concentrated upon the expected location of the benzene plume, toluene and p- and o-xylene were found at higher concentrations than benzene. Perhaps the bulk of the benzene plume had migrated beyond

Table 2.5: Predicted Maximum BTX Concentrations in the Non-Biotransformable BTX Plumes

Time Since Injection (days)	Plume Length (m)[1]	Maximum benzene (ng/L)	Concentrations toluene or xylenes (ng/L)
273	1		2000[2]
434	1.4	1000[2]	1430
656	2.9	480	690
750	8.7	160	230

1 - relative to the length on day 273 which is arbitrarily assigned a length of 1 m.
2 - assumed to be about the GC analytical detection limit

the sampled network and the samplings found the more retarded toluene and xylene plumes.

For all the monoaromatics, the concentrations found on day 750 were lower than the maximum expected concentrations. Perhaps the maximum concentrations present in the groundwater were distributed erratically and were missed. Given the uncertainty in calculating the concentrations expected due to dispersive dilution of a non-biotransformable BTX plume, the differences may not be significant. The BTX concentrations appear erratic, much like the benzene concentrations from day 396 to day 434.

If the observed concentrations on day 750 are representative, they are significantly lower than the expected concentrations resulting from dispersion only (Table 2.5). Then it must be concluded that biotransformation of BTX continues below ug/L concentrations.

Chapter III

REMEDIATION OF GASOLINE-CONTAMINATED GROUNDWATER

3.1 BACKGROUND AND APPROACH FOR THE FIELD EXPERIMENT

Following a gasoline spill on ground surface, gasoline infiltrates the vadose zone, moving down towards the water table. As the gasoline migrates downwards, an immiscible residue is left behind. Depending upon the extent of the spill, gasoline in the subsurface may be limited to the residual phase in the vadose zone or it may also form a pool of free product which floats on top of the saturated zone. Figure 3.1 illustrates the possible distribution of gasoline constituents following a surface spill. Both the residual gasoline and the free product may act as source for solubilization of gasoline constituents into the groundwater.

Following a gasoline spill or leakage, hydraulic recovery of the gasoline phase from the top of the saturated zone is commonly employed at the contaminated site. Soil containing residual gasoline is excavated when possible. There are a number of techniques which may be used to treat the groundwater and clean up the aquifer. Remedial measures commonly employed include withdrawal of the groundwater with subsequent physical, chemical, or biological treatment on surface. Alternatively, the contaminated water may be treated in situ.

In order for in situ remediation to be successful, the behaviour of BTEX in groundwater must be established. The mobility of any dissolved organic compounds in groundwater is controlled by many physical, chemical, and biological processes. The dominant physical processes controlling the mobility of any solute are advection and dispersion. These are discussed in detail in Gillham and Cherry (1982). Although dilution due to dispersion is a form of attenuation, it alone is usually unsuitable for the remediation of gasoline-contaminated water. The extremely low drinking water standards necessitate dilution of gasoline-contaminated water by factors of 10^4 to 10^5. This could only be achieved at great distances from the source of contamination.

In addition, organic solutes are subjected to a number of chemical and biological processes. The important chemical process controlling the behaviour of BTEX in groundwater is sorption. Descriptions of the nature of the sorption processes are given by Cherry et al. (1984) and Karickhoff (1984). Sorption may serve to remove some BTEX from contaminated water, however, this process is reversible (Patrick et al., 1985) and therefore not a viable means of remediation of BTEX.

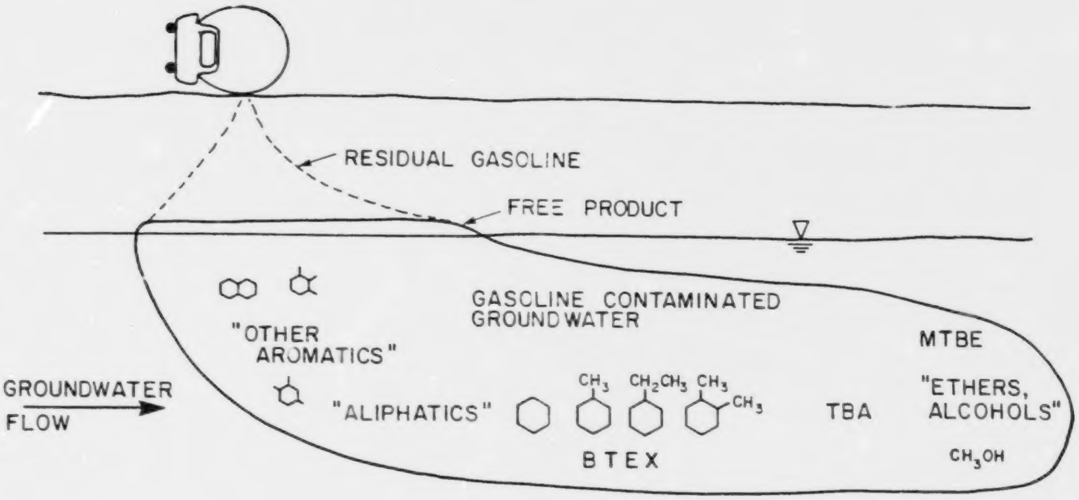

RESIDUAL GASOLINE
FREE PRODUCT
GASOLINE CONTAMINATED GROUNDWATER
"OTHER AROMATICS"
MTBE
GROUNDWATER FLOW
"ALIPHATICS"
CH3 CH2CH3 CH3
CH3
TBA
"ETHERS, ALCOHOLS"
BTEX
CH3OH

Figure 3.1: Distribution of gasoline following a spill (after Schwille, 1984)

Biodegradation, the biological process of interest, represents the most favourable form of attenuation of gasoline constituents in groundwater because it is irreversible and can result in the production of innocuous products. Recent research has shown that a significant bacterial population exists within the subsurface (Ghiorse and Balkwill, 1983). Although the addition of acclimated microorganisms to contaminated aquifers is a current biorestoration practise, there is little documented evidence to support the advantage of these organisms over the acclimated indigenous organisms (Wilson et al., 1986). Fortunately, the monoaromatic hydrocarbons can be biodegraded by naturally occurring bacteria (Gibson and Subramanian, 1984).

Several researchers have shown that the pure dissolved compounds benzene, toluene, and xylene isomers (termed BTX) will degrade in the presence of oxygen. Wilson et al. (1983) and Major et al. (1988) have conducted laboratory experiments using aquifer material and groundwater and have found that BTX does degrade aerobically. Patrick et al. (1986) demonstrated that this biodegradation mechanism could reduce benzene, toluene and xylenes (BTX) concentrations in the groundwater of a shallow sand aquifer to below 1-2 ppb levels within 410 days. Oxygen in the groundwater environment is limited to that which is dissolved in the water, 8 to 15 mg/L maximum. In the previous field experiment, Patrick et al. (1986) found the major limitation of BTX biodegradation to be the availability of dissolved oxygen. Oxygen became depleted, even in this aerobic groundwater environment, because it was consumed during BTX biodegradation. Where the oxygen demand of the BTX exceeded the available oxygen, BTX persisted. Eventually, dispersion brought BTX-contaminated waters into contact with sufficient oxygenated waters to produce the essentially complete removal of BTX via biodegradation.

Where large volumes of groundwater are contaminated by gasoline, oxygenation of the contamination by the dispersive processes may be inadequate to produce sufficiently rapid attenuation. In situ remedial measures commonly employed in such cases include the addition of oxygen or oxidizing agents (peroxide or ozone) to the groundwater.

Another potential in situ remedial scheme is the addition of nitrate to the gasoline-contaminated groundwater. Nitrate has some advantages over oxygen as an electron acceptor (oxidant) in such remedial schemes. It is much more soluble than oxygen, so high levels of contamination can be treated with nitrate addition. This advantage over oxygen is shared by peroxide. However, strong oxidants such as peroxide and oxygen can also bring about detrimental geochemical changes. For example, dissolved iron may be oxidized by oxygen and precipitated as iron oxyhydroxides which reduce aquifer permeability. Nitrate is less likely to produce such radical geochemical changes. On the other hand, nitrate is a recognized contaminant and so its fate must also be established in order to protect groundwater quality.

Kuhn et al. (1985) found that xylene isomers were degraded during denitrifying conditions in laboratory columns of material from an aquifer/river bed interface. Zeyer et al. (1986) found that m-xylene and toluene were rapidly mineralized during denitrification in columns containing aquifer material. However, Bouwer and McCarty (1984) found that ethyl benzene was not degraded under denitrifying conditions by sewage effluent organisms.

The general objectives of this portion of the research were twofold:

1. to assess nitrate addition as an in situ remedial technique for gasoline-contaminated groundwater

2. to assess the impact of other non-BTEX dissolved gasoline constituents on the mobility and biodegradation of BTEX in groundwater.

These general objectives were addressed by conducting a series of laboratory and field experiments. The specific tasks for the first general objective were:

1. to determine if nitrate can be mixed with existing gasoline contamination in groundwater within an aquifer (i.e. in situ) under natural gradient conditions simply by solute transport mechanisms

2. to evaluate nitrate addition during oxygen-limited conditions as a means of enhancing BTEX biodegradation by naturally occurring microorganisms in an aquifer-groundwater environment in laboratory and field environments

3. to compare the results of laboratory and field experiments.

The second general objective was addressed by comparing the behaviour of gasoline-derived BTEX with the behaviour of BTX dissolved from pure compounds. The specific tasks for the second objective were:

1. to compare biodegradation rates of pure BTX dissolved in water and gasoline-derived BTEX inlaboratory microcosms

2. to compare retardation and mass removal of BTX and BTEX in the field.

3. to compare the differences and similarities obtained in laboratory studies with those obtained from the field experiment.

A controlled field experiment was performed and involved the injection of two volumes or slugs of gasoline-contaminated groundwater below the water table as two simultaneous, parallel, uniform pulses. Up gradient from these slugs, a second injection was performed. Behind one gasoline slug (referred to hereafter as the remediated slug), groundwater containing nitrate was introduced while unmodified groundwater was introduced upgradient of the other slug (unremediated control). It was anticipated that the gasoline constituents would migrate at 65 to 90% of the groundwater velocity due to sorption (Patrick et al., 1985) and would be overtaken by nitrate which migrates at the groundwater velocity. Nitrate addition as an in situ remediation of gasoline-contaminated groundwater was evaluated following comparison of changes in distribution and total mass of the BTEX components of the contamination in both the unremediated and remediated experiments. The impact of dissolved non-BTEX gasoline components on the behaviour of BTEX in groundwater was assessed by comparing the persistence and mobility of BTEX in the unremediated control with BTX as described by Patrick et al. (1986).

3.2 DENITRIFICATION AND BIODEGRADATION OF AROMATIC COMPOUNDS

Evans (1977) summarizes three general processes by which catabolism (or degradation) of organic compounds may occur: 1. aerobic respiration - molecular oxygen is used as the terminal electron acceptor and is also incorporated into the mineralization products (carbon dioxide and water), 2. anaerobic respiration - nitrate, sulphate or carbon dioxide may be used in place of oxygen as the electron acceptor and are reduced to nitrogen gas, sulphide ion, or methane, 3. fermentation - no external electron accceptor is required during degradation of a carbon source.

Although the biochemical pathways are usually the same for aerobic and anaerobic respiration with the only difference being the terminal electron acceptor, this is not so for aromatic hydrocarbons (Evans, 1977). The difference in biochemical pathways is due to the manner by which the aromatic ring structure is cleaved. In the presence of oxygen, bacteria use enzymes called oxygenases to cleave the benzene ring. However, these enzymes are not activated in the absence of oxygen and thus ring cleavage cannot occur in this manner. This fundamental difference in biochemical breakdown pathways has prompted much research in the field of aromatic degradation. However, the precise biochemical fate of the aromatic hydrocarbons in the presence of denitrifying bateria and nitrate is unknown.

Denitrification, by definition, is the biological production of gaseous nitrogen(N_2,N_2O) by dissimilatory reduction of ionic nitrogenous oxides (NO^{3-},NO^{2-}) (Tiedje, 1982). The reduction is believed to be stepwise as indicated in Figure 3.2 and is accomplished by a complex suite of enzymes associated only with denitrifying bacteria. It represents a form of anaerobic respiration in which an organic carbon source is oxidized (or degraded) while nitrate or nitrite is reduced. Denitrifying bacteria are facultative anaerobes and preferably utilize oxygen as an electron acceptor when it is available (Tiedje, 1982).

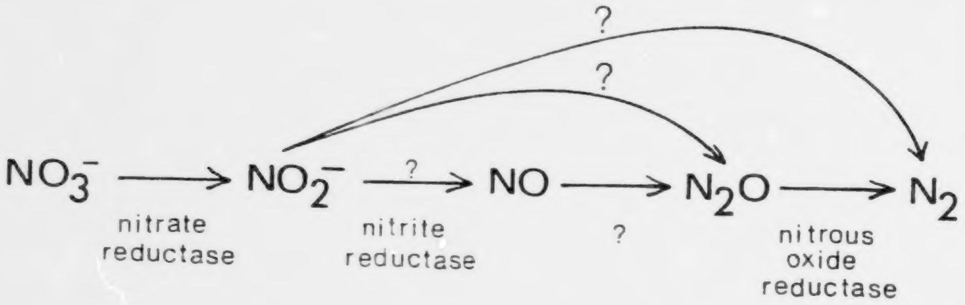


Figure 3.2: Enzymatically controlled denitrification steps

The rate of denitrification is controlled by the amount of oxygen present, organic carbon type, and the pH and temperature of the water (Knowles, 1982). Oxygen has an inhibitory effect on nitrogen oxide reductases. During investigation of denitrification in shallow sand aquifers, Gillham and Cherry (1978) found denitrification occurred in groundwater only when dissolved oxygen levels were below 2.0 mg/L. More recently, evidence was presented which suggests denitrification can occur in the presence of considerable amounts of oxygen (Lloyd et al., 1987). The occurrence of denitrification, an anaerobic proccess, during aerobic conditions may be explained by invoking anaerobic microsites. The microenvironment of metabolically active bacteria may be quite different than perceived from analysis of water samples because of the high flux of solutes to and from the bacteria. Anaerobic microsites may occur if oxygen is absent within the micro-environment of bacteria.

The environmental conditions, especially pH and temperature, may be impossible to modify in the groundwater and aquifer system. Although the conditions present may not be conducive to optimum denitrification rates for all denitrifiers, the bacteria present within the aquifer system are adapted to survive in these less than perfect conditions. Modification of these conditions may not produce favourable changes in the denitrifying ability of the aquifer's microbes.

Nitrate may be biologically reduced by alternative means. It may be reduced to nitrite and then to ammonia during the synthesis of amino acids (Payne, 1973). This process is referred to as assimilatory reduction and may occur under either aerobic or anaerobic conditions. Nitrate may also undergo dissimilatory reduction to ammonium. Organisms with this ability are usually strict anaerobes which are capable of fermentation and anaerobic growth (Tiedje, 1982). Dissimilatory reduction of nitrate to ammonium was found to be an important process causing nitrate losses in laboratory experiments using estuarine sediments (Keith et al., 1982), river sediments (Hill and Sanmugadas, 1985) and sewage sludge (Kaspar et al., 1981). Samuelson (1985) provides evidence for the simultaneous reduction of nitrate to nitrite and ammonium by a single pure denitrifying culture. Thus reduction of nitrate to ammonium may occur within the same habitat as denitrification.

Nitrate losses in the groundwater environment may be the result of assimilation, dissimilatory reduction to ammonium, or denitrification. Losses due to denitrification may be determined experimentally by using an acetylene block technique. Acetylene inhibits the reduction of nitrous oxide to nitrogen gas and denitrification rates can be experimentally determined from the rate of nitrous oxide accumulation (Tiedje, 1982). In this way, nitrate losses due to denitrification can be differentiated from losses due to other reductive processes.

3.3 LABORATORY BIOTRANSFORMATION EXPERIMENTS

Laboratory experiments were designed and initiated to investigate the transformation of pure dissolved BTX and gasoline-derived BTEX under various aerobic and anaerobic conditions. The purpose of these experiments was to help define the biological transformation processes and rates expected to occur during the field experiment. The experiments made use of microcosms - sealed bottles containing aquifer material and groundwater. Although these bottled systems are simple and static, they are thought to be representative of the biodegradation processes occurring within the groundwater environment (Pritchard and Bourquin, 1984). Thus, transformation processes were examined without the complication of solute transport.

Experiment 1 was conducted to examine the transformation of BTX under anaerobic and aerobic conditions in both the presence and absence of easily utilizable organic compounds. Experiment 2 examined the transformation of gasoline-derived BTEX during denitrification. The mineralization of benzene during aerobic and anaerobic conditions was examined in Experiment 3 through the use of radiocarbon labelling. Experiment 4 was conducted to compare aerobic biodegradation rates obtained for BTX and gasoline-derived BTEX.

Another group of experiments was conducted using a flow-through sand packed column simulating one-dimensional flow through porous media. The dynamic aspect of the flow-through column was similar to the dynamic field experiment. The column experiment differed from the field experiment in that the column used a constant source of BTEX instead of a slug input as in the field. This experiment was conducted to examine BTEX transformations during combined aerobic and denitrifying conditions, a situation similar to the field experiment.

3.3.1 Materials and Methods

Four types of aquifer material were used as inoculum for these experiments: uncontaminated material (type 1), aquifer material previously exposed to BTEX during the Phase III field experiment (type 2), aquifer material previously exposed to BTEX and nitrate during that same field experiment (type 3) and aquifer material exposed to BTX during the Phase II experiment (type 4). Aquifer material was obtained from cores taken from the Borden field site at an approximate depth interval of 1.4 to 3.4 m. Type 1 material was taken aseptically from a saturated core obtained from an uncontaminated area of the aquifer about 5 m east of the experimental area. Material types 2 and 3 were obtained by coring the aquifer approximately 6 m upgradient from the last known location of each BTEX slug during the Phase III field experiment. In this way, aquifer material was obtained that had been exposed to BTEX approximately 60 days prior to coring. Type 3 material had pore water which contained nitrate at concentrations above background. Material type 4 was obtained by coring the aquifer upgradient from the last known location of the BTX slug of Patrick et al. (1986). The cores were capped and sealed to prevent atmospheric exposure and were stored at 4^0C.

BTEX-free groundwater was obtained from the same well that was used as a source for the preparation of injection solutions for the field experiment (see Appendix A). After retrieval, the water contained about 3.5 mg/L dissolved oxygen (D.O.) but this usually increased during storage.

Gasoline-saturated water was used as a source of BTEX for the microcosm experiments. Groundwater and unleaded gasoline, at an approximate volume ratio of 7:1 (water:gasoline), were added to a separatory funnel. Over 15 minutes, the funnel was periodically shaken manually. The gasoline and water mixture was allowed to equillibrate for 12 hours before dispensing the water phase which contained approximately 65 mg/L total BTEX in a concentration ratio of 4:7:1:1:2.5:2 (benzene:toluene:ethyl benzene:p-xylene:m-xylene:o-xylene).

Table 3.1 lists the major compounds identified in gasoline-saturated water (Brookman et al., 1985). Of these, BTEX comprise about 60% of the total identified concentration. Analyses of gasoline-contaminated water in the Organic Geochemistry Laboratory at the University of Waterloo revealed the presence of butyl alcohol, methyl propyl hydroxylamine, propyl benzene, hydroxy benzenesulfonic acid, napthalene, methyl pentene, cylcopentadiene and dimethyl cyclopropane in addition to those listed in Table 3.1. These were identified using an acid extraction technique (EPA Method 625) and gas chromatrography-mass spectrometry (GCMS) with detection limits of about 0.5 ug/L.

Table 3.1: Compounds identified in gasoline-saturated water at concentrations >1 mg/L (Brookman et al., 1985).

COMPOUND	CONC.	ANALYTICAL METHOD
Benzene	63	1
Toluene	38	1,3
Ethyl Benzene	4	1,3
Butane	5.4	1
Butene	1.1	1
Methyl Butane	5.0	1
Pentane Isomers	4.0	1
Pentene Isomers	6.4	1
Cyclopentene	1.0	1
Methyl Phenol Isomers	34	2
Dimethyl Phenol Isomers	9.5	2
Ethyl Phenol	1.0	2
Xylene Isomers	11	3
Ethyl Methyl Benzene	1.0	3
Trimethyl Benzene Isomers	1.2	3

Analytical Methods (details given by Brookman et al., 1985)
1 - volatile scan
2 - acid extraction
2 - base/neutral extraction

Microcosms were normally established in 60 cm^3 glass hypovials, sealed with teflon-faced silica septa and aluminum seals or teflon mininert valves (Pierce Chemical Co., Rockford, Il.) After capping, the microcosms were incubated in the dark at 10^0C, the average groundwater temperature at Borden. Control microcosms, in which no biological activity was assumed to occur, were analyzed with the active microcosms to monitor the non-biological processes (for example, diffusion, sorption) affecting BTEX. Controls were established by autoclaving the aquifer material on three consecutive days and poisoning with 0.6 cm^3 of a 10% sodium azide solution or 2.4 cm^3 of a 7.4% mercuric chloride solution. Sterility of the controls was checked by periodically performing spread plate counts using the aquifer material of the control microcosm as inoculum. The plate count technique and analytical methods are described in Appendix B.

3.3.2 Experiment 1:Effect of Terminal Electron Acceptors and Primary Substrates on the Mass Loss of BTX

Experiment 1 was conducted to determine if biodegradation of BTX could be induced under anaerobic conditions. Aromatic degradation has been found to occur anaerobically under very strongly reducing conditions (Vogel and Grbic-Galic, 1986; Wilson et al., 1986; Grbic-Galic and Vogel,1987), and by denitrification (Kuhn et al., 1985, Zeyer et al., 1986). Nitrate was added to anaerobic microcosms and was intended to serve as the alternate electron acceptor to oxygen. Primary substrates, added to stimulate secondary substrate utilization (Rittman et al., 1980; McCarty et al., 1981) of BTX, were simple fermentable organic compounds that are metabolized by methanogens, sulfate-reducers and strict anaerobic microorganisms. It was anticipated that these populations, if present in the aquifer material, would be stimulated by the addition of these primary substrates, and the organisms would subsequently degrade BTX either directly or as secondary substrates.

Thirty-two microcosms were set up in an anaerobic glovebox. Type 4 aquifer material, groundwater and other equipment were purged overnight with filtered oxygen-free nitrogen gas. Twenty-five grams of core material were placed into sterile hypovials which were then filled completely with reduced, room temperature groundwater. Teflon mininert valves were installed so as to eliminate any gaseous headspace. The dissolved oxygen concentration (D.O.) of the groundwater was checked at the beginning, middle and end of the set up and all samples indicated initial oxygen levels below the detection limit (about 0.2 mg/L).

The microorganisms present in the aquifer material are likely oligotrophic (capable of growth at low carbon concentrations) and adapted to the low aquifer temperatures. The establishment of the microcosms at room temperature would have disrupted the population ecology and the addition of BTX at this time could be detrimental to the surviving population. Although steps were taken to minimize the contamination of the microcosms by surface microorganisms, the possibility of contamination could not be completely excluded. Hence, the microcosms were incubated anaerobically at 10^0C for six weeks for two reasons: to allow re-establishment of "normal" microbial populations before exposure to BTX and to take advantage of oligotrophic conditions to select against any surface organisms that may have been introduced.

Equal volumes of pure benzene, toluene, o- and m-xylene were mixed and 0.6 ul added to twenty non-sterile and to two sterile microcosms to give an initial concentration of each compound of 3 mg/L. The remaining ten microcosms did not received any further treatment. Of the remaining twenty microcosms, four received acetate to give a concentration of 100 mg/L, four received lactate (100 mg/L), four received formate (100 mg/L), four received sodium nitrate (100 mg/L as NO_3^-) and four received no further amendments. Half the microcosms had an additional 0.25 cm^3 of pure oxygen added to establish aerobic conditions. Samples from each microcosm were periodically taken through the septum of the mininert valve and BTX was analyzed by HPLC (Patrick et al., 1986, Appendix A). A pair of microcosms were periodically sacrificed for oxygen determinations.

Table 3.2 summarizes the disappearance of the BTX under the anaerobic and aerobic conditions. Figure 3.3 shows benzene disappearance under the various treatments. Other aromatics demonstrated similar disappearances. All microcosms, including the sterile controls, exhibited an initial mass loss of approximately 20%, probably due to sorption of BTX to the aquifer material. After 62 days, anaerobic microcosms containing nitrate showed significant utilization of all four aromatic compounds relative to the sterile control. The addition of primary substrates (acetate, formate and lactate) under anaerobic or aerobic conditions in order to promote secondary substrate utilization did not significantly enhance the disappearance of BTX (Table 3.2). The active anaerobic microcosms showed an additional mass loss of 20-30% of BTX compared to the sterile control. Microcosms receiving nitrate only, oxygen only, and both nitrate and oxygen show similar BTX concentrations after 62 days (Table 3.2). The BTX biodegradation rate was 0.1 to 0.2 mg/L.d. Figure 3.3 shows similar benzene loss for these three microcosm types. It was concluded from these results that BTX was removed anaerobically in the presence of nitrate. A complete discussion of the results of this experiment is provided by Major et al. (1988).

Table 3.2: BTX remaining after incubation for 62 days with various additions under aerobic and anaerobic conditions. Initial concentration for each compound was 3 mg/L.

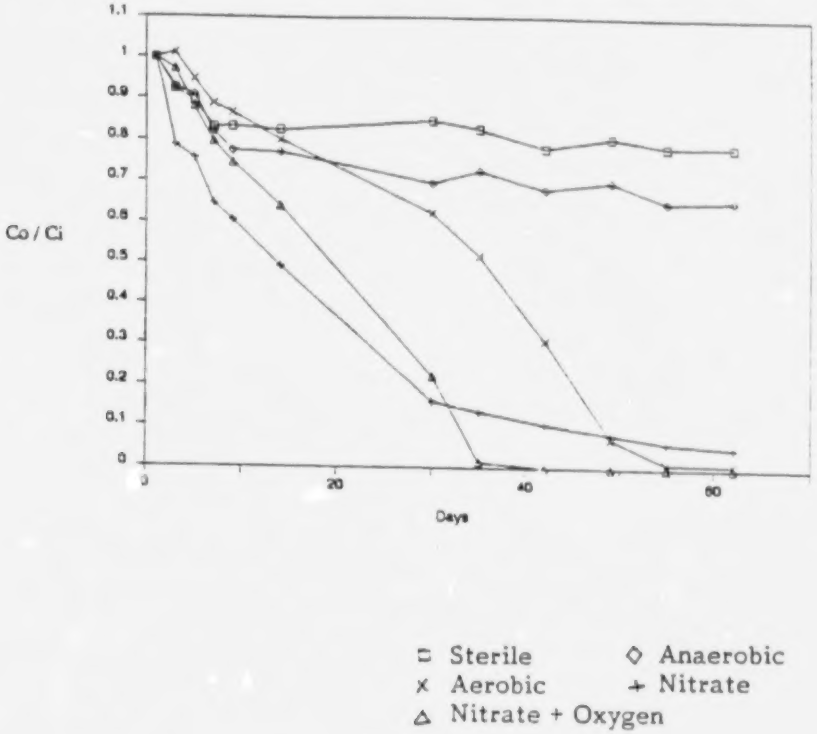
PERCENT REMAINING

	CONDITION										
	Anaerobic						Aerobic				
	St	Nit	Ace	Lac	For	Blk	Nit	Ace	Lac	For	Blk
COMPOUND											
Benzene	79	5	63	57	62	66	0	53	65	67	1
Toluene	86	2	63	55	58	65	0	54	63	63	0
O-xylene	80	15	65	53	61	73	13	57	63	66	15
M-xylene	80	12	51	46	40	59	8	41	49	56	11

St - sterile
Nit - nitrate
Ace - acetate
Lac - lactate
For - formate
Blk - no additions

The most promising information obtained from this experiment is the mass loss of BTX after the addition of nitrate. Since nitrate stimulated BTX removal under anoxic conditions, the addition of nitrate to anoxic groundwater might be an adjunct to the methods currently used to remediate gasoline-contaminated waters. In the previous field experiment, Patrick et al. (1986) demonstrated the persis-

Figure 3.3: Benzene mass loss under various treatments.. Concentrations are normalized by dividing by concentration found in the sterile controls.



tence of BTX in zones of limited oxygen. Addition of nitrate would allow biodegradation to occur in the anoxic zones within the BTX plume. This remedial technique was attempted in the field experiment to be described later.

3.3.3 Experiment 2 - BTEX Transformations during Denitrification

This experiment was conducted to assess BTEX transformations under anaerobic denitrifying conditions. Microcosms contained aquifer material, groundwater, BTEX from gasoline, nitrate and acetylene. The concentrations of BTEX, nitrate and nitrous oxide were monitored through time.

Microcosms were established in 60 cm^3 hypovials, each containing 13 g of either uncontaminated (type 1) or BTEX and nitrate exposed (type 3) aquifer material. Groundwater was purged with nitrogen gas to reduce the dissolved oxygen concentration from 3.5 to less than 1.0 mg/L. Oxygen-free gasoline-saturated water was used to spike this anaerobic groundwater to a total BTEX concentration of about 2.6 mg/L.

The denitrification reaction utilizing toluene as a carbon source can be written as:

$$C_7H_8 + 7.2H^+ + 7.2NO_3^- \dashrightarrow 3.6N_2 + 7.6H_2O + 7CO_2 \qquad (1)$$

To ensure sufficient nitrate was available for the denitrification reaction to proceed to completion, the nitrate demand was calculated for the solution containing BTEX according to (1). Potassium nitrate was added to the water to give a nitrogen concentration of 5.5 mg/L, twice the calculated nitrate demand. Acetylene gas was added to the water to give a concentration of 5.4% by volume. After stirring for one hour, the solution was poured into the microcosms within an anaerobic glove box leaving no entrapped headspace. After capping, all hypovials were incubated in anaerobic jars. At various times, duplicates of control and active microcosms of each aquifer material type were sacrificed for BTEX, nitrate and nitrous oxide analyses (Appendix B).

After near depletion of nitrate in the active hypovials by day 122, 0.1 cm^3 of a 17.3% potassium nitrate solution was added to the remaining control and active microcosms through the septa by syringe. The pierced septa were sealed with silicon. The hypovials were inverted to help prevent losses through the puncture and stored again in oxygen-free containers.

The results from microcosms containing uncontaminated (type 1) aquifer material are presented in Figures 3.4 and 3.5. The concentration values shown were derived from averaging the results obtained from duplicate microcosms. Variation between duplicate microcosms was generally less than 10%. Results obtained from microcosms containing type 3 aquifer material were similar to the results shown in Figures 3.4 and 3.5.

Control microcosms remained inactive during the initial 50 days, however, gas production occurred after this. Sterility of the controls was confirmed at this point and the gas production was assumed to be a chemical reaction possibly involving mercuric chloride. Unfortunately, the gas was not identified. BTEX losses were evident in some of the control microcosms and may have been due to their involvement in the reaction.

Nitrate losses were detected in active microcosms after 10 days and were simultaneous with nitrous oxide accumulations (Figure 3.4), indicating denitrification was the process responsible for at least some of the nitrate loss. Nitrous oxide concentrations increased to a maximum at day 76 and decreased afterwards. After addition of more nitrate on day 138, nitrous oxide production resumed.

Nitrogen mass balances were performed using the data for individual active microcosms to examine nitrate losses. Table 3.3 lists the predicted nitrous oxide production for microcosms assuming that all observed nitrate losses resulted in nitrous oxide production. The ratio of measured to predicted nitrous oxide con-

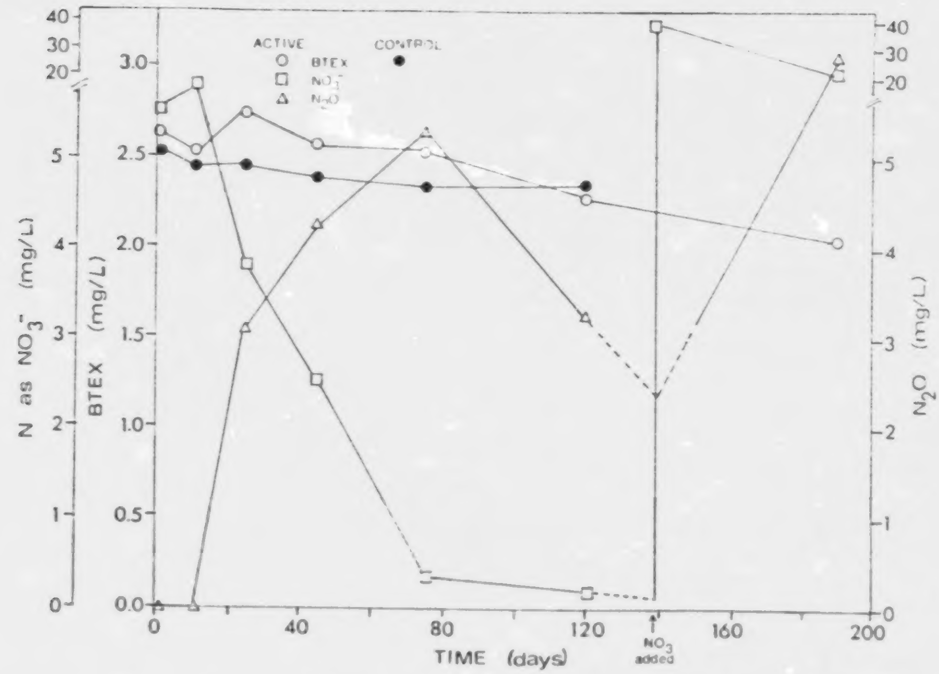


Figure 3.4: Observed BTEX, NO_3^-, and N_2O concentrations in active and control microcosms of Experiment 2

centrations decreased with time to day 122 suggesting either nitrous oxide was lost or some nitrate was lost by processes other than denitrification. Several explanations for this trend are listed below:

1. Although acetylene was added to the microcosms to block the enzymes responsible for the reduction of nitrous oxide, it is not known for how long or under what conditions this block remains effective. Perhaps as the concentration of nitrate became depleted at day 122, denitrifying bacteria were no longer inhibited by acetylene and were able to reduce nitrous oxide to nitrogen gas.

2. A black precipitate had formed on the sand surface by day 76 was assumed to be iron sulfide. The inhibitory effects of acetylene may be limited in the presence of sulfide (Evans et al., 1985).

3. Nitrous oxide may have diffused out of the hypovials.

4. Nitrogen assimilation by the bacteria may have increased with time causing additional nitrate losses.

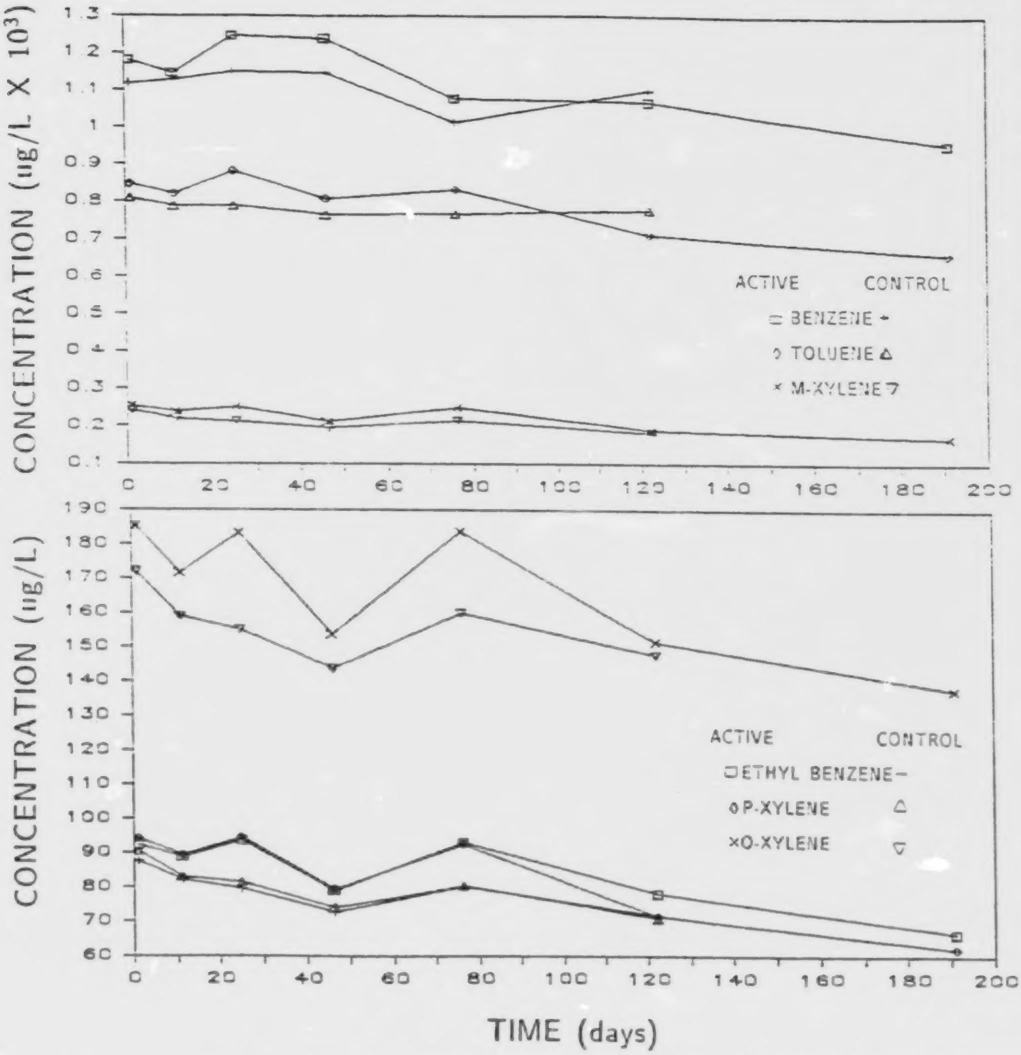


Figure 3.5: Observed BTEX concentrations in active and control microcosms of Experiment 2

The total BTEX removed over 191 days was 0.5 mg/L or about 20% of the initial BTEX. It is not certain when BTEX losses began because of the fluctuation of both active and control BTEX concentrations in Figures 3.4 and 3.5. These fluctuations are due in part to analytical uncertainties as well as sorptive losses of BTEX. It may be argued that BTEX removal commenced immediately and continued at a slow rate for 191 days, or alternatively, that BTEX removal did not commence until after 76 days when BTEX concentrations in active microcosms show definite losses relative to controls. Whichever the interpretation, the main point here is that BTEX removal was very slow, less than 10 ug/L.d (0.010 mg/L.d). This removal rate is an order of magnitude less than the BTX removal rate reported for anaerobic conditions in Experiment 1.

The observed BTEX losses of about 0.5 mg/L cannot account for the total nitrate losses which were in excess of 20 mg/L (N as NO_3^-). Although other gasoline constituents were also present with BTEX in the groundwater, it seems unlikely that these would have a nitrogen demand approximately ten times that of BTEX. The naturally occurring organic carbon associated with the groundwater or aquifer material may have been involved. If it is assumed that the organic carbon in groundwater is in the form of carbohydrates, the denitrification reaction can be written as (Stumm and Morgan, 1981):

$$5CH_2O + 4NO_3^- + 4H^+ \longrightarrow 2N_2 + 5CO_2 + 7H_2O \qquad (2)$$

From this stoichiometry, 1 mg of nitrogen from nitrate reactes with 0.93 mg of organic carbon. Borden groundwater was found to have a naturally occurring total organic carbon content (T.O.C.) of 5 to 7 mg/L. The nitrate losses of about 20 mg/L were much greater than expected if this T.O.C. were the only carbon source degraded.

Denitrifying bacteria have been recognized to utilize the solid organic matter found in aquifer material at other sites (R. Starr, Univ. of Waterloo, pers. commun.) Borden aquifer material has an organic carbon content (f_{OC}) of .02% (Patrick et al., 1985). For a 60 cm^3 microcosm containing 13 g of aquifer material, the nitrogen demand for denitrification utilizing this organic carbon could be as high as 43 mg/L.

In summary, denitrification occurred in oxygen deficient Borden aquifer material when dissolved gasoline constituents were present. BTEX removal during denitrification was slight and the rates of removal were extremely slow. Denitrifying bacteria utilized other sources of organic carbon. The use of naturally occurring organic matter in the aquifer material by denitrifying bacteria is suspected.

Table 3.3: Nitrogen Mass Balance Calculations

DAY	AQUIFER MATERIAL	NO_3^--N (mg/L)	ACTUAL N_2O (mg/L)	PREDICTED N_2O (mg/L)	RATIO OF ACTUAL TO PREDICTED N_2O
4	uncont'd	5.72	-		
		5.90	-		
	exposed	5.72	-		
		5.77			
25	uncont'd	3.19	3.36	3.62	0.93
		4.45	2.85	1.64	1.73
	exposed	5.79	0.47	-0.46	-1.03
		5.35	0.75	0.23	3.18
46	uncont'd	4.41	1.46	1.71	0.85
		0.60	7.09	7.69	0.92
	exposed	0.46	5.90	7.91	0.74
		4.31	1.43	1.87	0.76
76	uncont'd	0.49	5.14	7.86	0.65
		0.18	5.07	8.35	0.61
	exposed	0.13	6.63	8.43	0.67
		3.24	2.83	3.55	0.79
122	uncont'd	0.11	2.85	8.46	0.34
		0.35	3.60	8.08	0.44
	exposed	0.19	3.93	8.34	0.51
		<0.05	4.28	8.55	0.50
191	uncont'd	29.1	20.7	17.10	1.21
		16.0	37.0	37.68	0.98
	exposed	1.93	40.9	59.76	0.68
		19.2	N.A.	32.65	N.A.

3.3.4 Experiment 3 - ^{14}C-Benzene Transformation

This experiment was conducted to confirm the mineralization of benzene to carbon dioxide and to investigate the relationship of nitrate utilization and benzene metabolism. Gasoline was added to several microcosm sets to simulate an actual spill and to determine the effects of the other water-soluble gasoline components on the biodegradation of benzene.

Seventy-two microcosms containing type 4 aquifer material and groundwater were divided into 10 groups as shown in Table 3.4. Periodically, one microcosm from each group was sacrificed for analysis. Dissolved oxygen concentrations were determined for aerobic microcosms. Radioactivity associated with benzene, carbon dioxide, and dissolved in the water (non-purgable, water-soluble organics) was determined using the method outlined in Appendix B. Nitrate, nitrite, ammonium and D.O. concentrations were also monitored. Analytical results are listed in Appendix D.

Benzene was mineralized to $^{14}CO_2$ in all non-sterile microcosms but the degree with which this occurred was dependant upon the additions. There was significant benzene biodegradation in the anaerobic microcosms not containing nitrate. The sand became very black and a strong H_2S odour was apparent after opening. This was also noted in microcosms for Experiment 2. Therefore, the anaerobic microorganisms reponsible for the degradation of benzene could have been sulfate reducers. There was an increase in the ^{14}C activity associated with the water phase in anaerobic microcosms while this activity diminished in the microcosms that received nitrate. This implies that benzene was degraded forming water soluble products which were then mineralized under denitrifying conditions.

The disappearance of nitrate and oxygen in microcosms which did not contain benzene indicates that a significant amount of utilizable carbon was associated with the aquifer material. In this experiment, the natural organic matter in the aquifer material interfere with the metabolism of benzene by serving as a competing source of carbon during denitrification. This is shown by the loss of nitrate and accumulation of nitrite in the microcoms containing only nitrate and is evident in microcosms containing benzene, nitrate with or without gasoline which showed an additional increase in $^{14}CO_2$ production after day 47 only when augmented with 1000 mg/L nitrate. No significant amounts of ammonia were detected during the course of the experiment indicating that assimilatory nitrate reduction was not operational.

Aerobic microcosms showed a rapid loss of oxygen, from a starting concentration of 7.7 mg/L to less than 1 mg/L within 4 days and can be considered anaerobic after day 7. Benzene losses were similar in anaerobic and aerobic microcosms. Again, there was oxygen lost in microcosms which did not contain any benzene indicating the presence of other metabolizable organic compounds in the microcosm.

Table 3.4: Microcosm Additions for Experiment 4.

A. AEROBIC
1. Sterile Microcosms
(i) none

2. Active Microcosms
(i) no additions
(ii) ^{14}C-Benzene only
(iii) ^{14}C-Benzene and gasoline

B. ANAEROBIC
1. Sterile Microcosms
(i) no additions
(ii) ^{14}C-Benzene and nitrate

2. Active Microcosms
(i) ^{14}C-Benzene only
(ii) Nitrate only
(iii) ^{14}C-Benzene and nitrate
(iv) ^{14}C-Benzene and gasoline
(v) ^{14}C-Benzene, nitrate and gasoline

INITIAL CONCENTRATIONS

PARAMETER	CONCENTRATION
^{14}-C	475 dpm/cm^3
nitrate	150 mg/L NO_3
unleaded gasoline	1 ul per microcosm
D.O.	7.7 mg/L

In summary, benzene was mineralized anaerobically in the presence and absence of nitrate. The biodegradation of benzene appeared to be conducted through an association between anaerobic and denitrifying microorganisms. Biodegradation products (non-purgable water-soluble organics) accumulated during anaerobic metabolism but were diminished when nitrate was added. Mineralization of benzene was more complete when nitrate was present.

3.3.5 Experiment 4 - The Effect of non-BTEX Compounds on BTEX Biodegradation

This experiment was conducted to directly compare the aerobic biodegradation of pure dissolved BTX and BTEX dissolved from gasoline. If biodegradation of toluene is complete, the reaction can be written as:

$$C_7H_8 + 9\,O_2 \text{ -----> } 7\,CO_2 + 4\,H_2O \qquad (3)$$

From this reaction, 1 mg of toluene requires 3.1 mg of oxygen for complete mineralization. Aerated groundwater containing a D.O. concentration of about 6 mg/L could theoretically be capable of removing a BTEX concentration of about 2 mg/L so 1 mg/L was set as the target total BTEX concentration to ensure oxygen limitation would not occur.

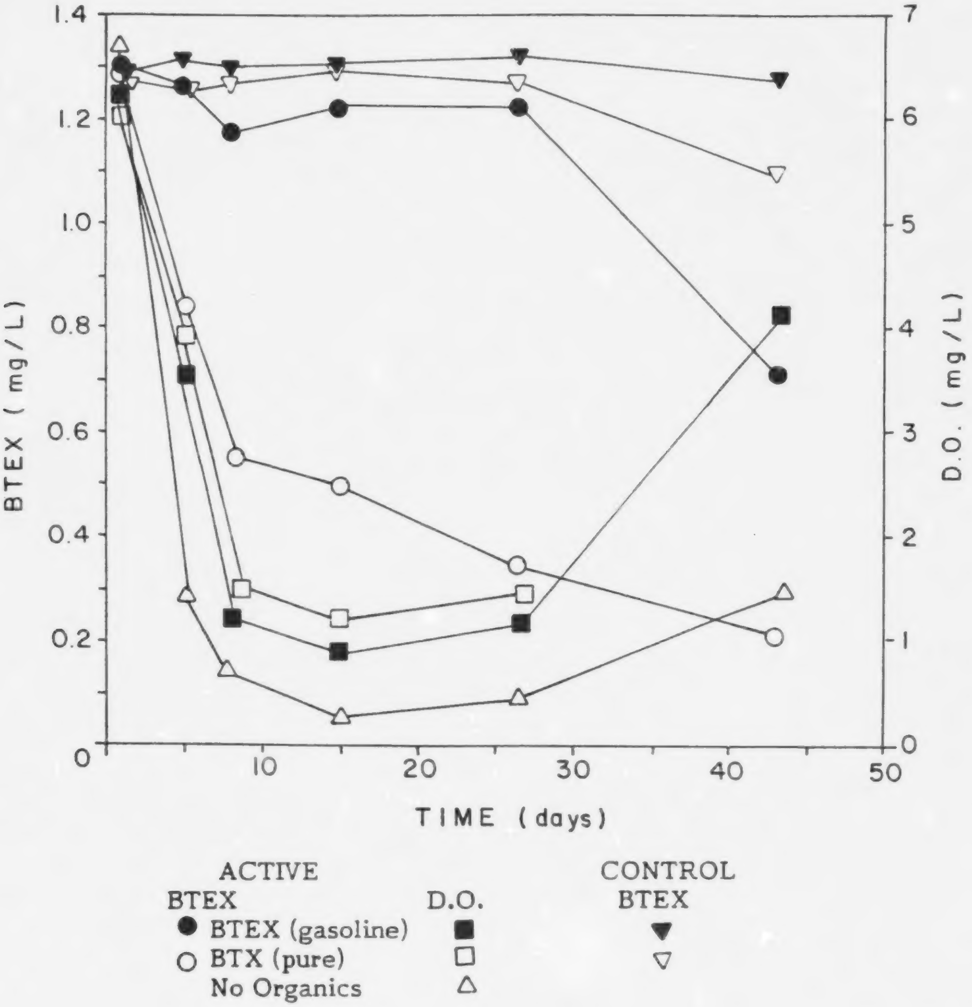
Aerated groundwater and 25 g of uncontaminated aquifer material (type 1) were added to each microcosm. One third of the microcosms received BTEX from gasoline at a concentration of about 1 mg/L. One third of the microcosms received pure BTX duplicating the concentrations of gasoline-derived BTEX. The remaining microcosms received no organic additions. All microcosms were incubated in anaerobic containers until oxygen-limiting conditions unexpectedly occurred after 27 days. Incubation continued after 28 days without storing in anaerobic jars so that oxygen could be supplied to the microcosms by diffusion through the septa.

At various times during the 43 day experiment, two active and two control microcosms of each type were analyzed for BTEX. Also, one active and control microcosm of each type was analyzed for dissolved oxygen. Although no changes in BTEX concentrations were evident for the controls, D.O. concentrations had decreased to less than 1.0 mg/L after 1 day. Sterility was confirmed so the nature of the oxygen utilization was concluded to be chemical oxidation. Figure 3.6 shows the change in total BTEX concentrations for active and control microcosms and the D.O. concentrations for active microcosms. Points represent the average of duplicate microcosms for organics and single D.O. determinations.

Active microcosms containing no added organic compounds showed a rapid decrease in D.O. concentrations during the first week. This is consistent with the results of Experiment 3. Oxygen may have diffused from the microcosms out into the anaerobic atmosphere but investigation of this process proved the diffusion rate to be much slower than the rate observed here. Biodegradation may have occurred by using the naturally occurring organic carbon in the groundwater or aquifer material. Alternatively, chemical oxidation may have caused the D.O. concentration decline. The oxygen demand of the aquifer material in the absence of added organic prevents the calculation of BTX and D.O. mass balances and biodegradation stoichiometry.

The BTX and corresponding D.O. concentrations decreased rapidly during the first week of the experiment. The rate of BTX removal decreased with time possibly due to oxygen limitation. The maximum rate of removal varied from 7

Figure 3.6: Concentrations of organics and oxygen in active and control microcosms of Experiment 4.



ug/L.d for o-xylene to 45 ug/L.d for toluene. These rates are consistent with BTX degradation rates reported by Barker et al. (1987) in which BTX degradation was controlled by oxygen diffusion into the microcosms and are consistent with BTX biodegradation rates commonly reported (Ward and Thomas, 1986).

During the first week, BTEX losses were small but corresponding D.O. decreases were similar to those observed in other microcosms. After about a month, BTEX concentrations were reduced in the two remaining duplicate microcosms. Significant removal of BTEX occurred only after 26 days but such an interpretation is based only upon the results obtained on day 43.

The period during which there was no noticeable degradation of BTEX is referred to as a lag period. The occurrence of a lag period has been attributed to many different causes including the time required for the necessary enzymes to be induced and the time for small mineralizing populations to become sufficiently large enough to produce detectable chemical losses (Wiggins et al., 1987 and references therein). The metabolism of aromatic compounds may be repressed by the presence of more easily metabolized compounds (Schmidt and Alexander, 1985; Harrison and Barker, 1987). The lag period may represent the time necessary to remove the preferred substrate to levels low enough to allow BTEX biodegradation to occur. Aliphatic hydrocarbons are present in gasoline-contaminated water. The non-aromatic nature of these compounds could certainly make them preferred to BTEX as sources of organic carbon.

The maximum rates of BTEX removal between two successive data points varied from 1 ug/L.d for ethyl benzene to 14 ug/L.d for toluene. These rates are one half to a full order of magnitude less than the BTX rates previously determined. The non-BTEX dissolved gasoline constituents slowed the degradation of BTEX substantially.

In summary, both pure dissolved BTX and BTEX from gasoline were biodegraded but BTX removal was greater than BTEX removal. This is in agreement with the results of Experiments 1 and 2. The stoichiometric relationships with oxygen are uncertain because of the high oxygen demand of the aquifer material alone. The presence of other dissolved gasoline constituents, along with BTEX, decreased the rate of BTEX utilization.

3.4 COLUMN EXPERIMENT

A column experiment was performed to study the biotransformation of BTEX under flowing water conditions. The column received a relatively high concentration of BTEX such that biodegradation would be limited by oxygen. After oxygen depletion, nitrate was added to the column in order to assess BTEX transformations under denitrifying conditions.

The experimental setup and sampling procedures are described in detail in Berry-Spark (1987). A plexiglass column (26 cm x 7.5 cm I.D.) was packed with type 2 Borden aquifer material. The columns were maintained at 10^0C, the average groundwater temperature at Borden. The influent solutions consisted of autoclaved gasoline-contaminated Borden groundwater which was in equilibrium with atmospheric oxygen. The influent BTEX concentration fluctuated because of volatilization within the 18 L glass storage jar and periodic respiking of the solution. Average input parameters for the experiment are listed in Table 3.5.

Samples of the effluent and influent solutions and small volume samples from the ports along the column length were collected and analyzed for BTEX, D.O., nitrate and nitrous oxide concentrations. Sample collection methods attempted to limit the exposure of the water to the atmosphere in order to minimize volatile losses and sample aeration.

Table 3.5: Experimental Parameters for Influent Solutions

Average Conc. (mg/L)	
BTEX	3118
D.O.	6.0
N as NO_3	23.6
Pumping Rate (ml/min)	0.8
(pore volume/day)	2.7
Velocity (m/day)	0.7

Results of the column experiment are presented as plots of time dependant effluent concentrations (or breakthrough curves) (Figures 3.7 to 3.9) and profiles which show the distribution of solutes along the length of the column at a given point in time (Figure 3.10).

After 20 days, the effluent contained 80% of the influent BTEX but only 20% of the influent D.O. The reduction of BTEX may be attributed to sorption or biodegradation. Further reduction of BTEX by aerobic biodegradation was limited by the low D.O. concentration (<1.0 mg/L).

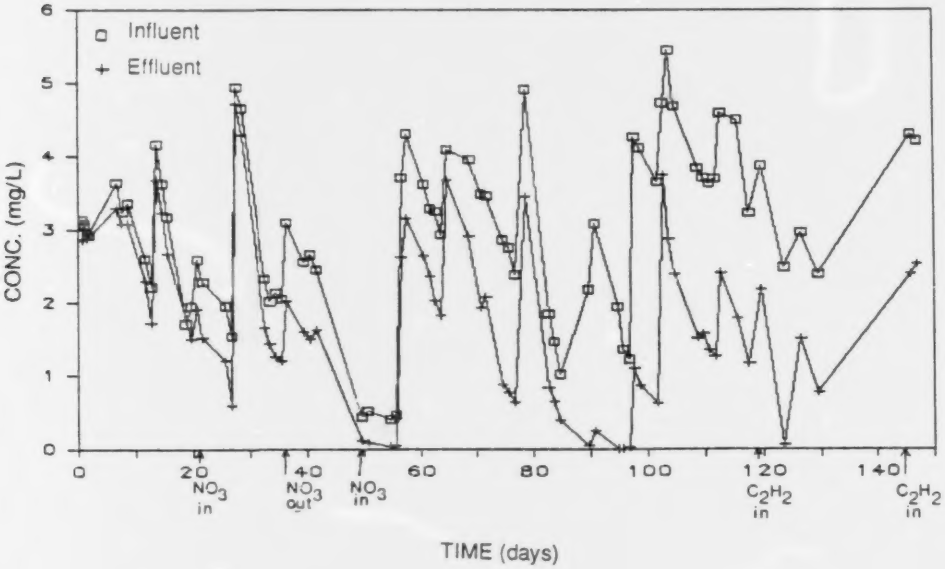


Figure 3.7: Influent and effluent BTEX concentrations.

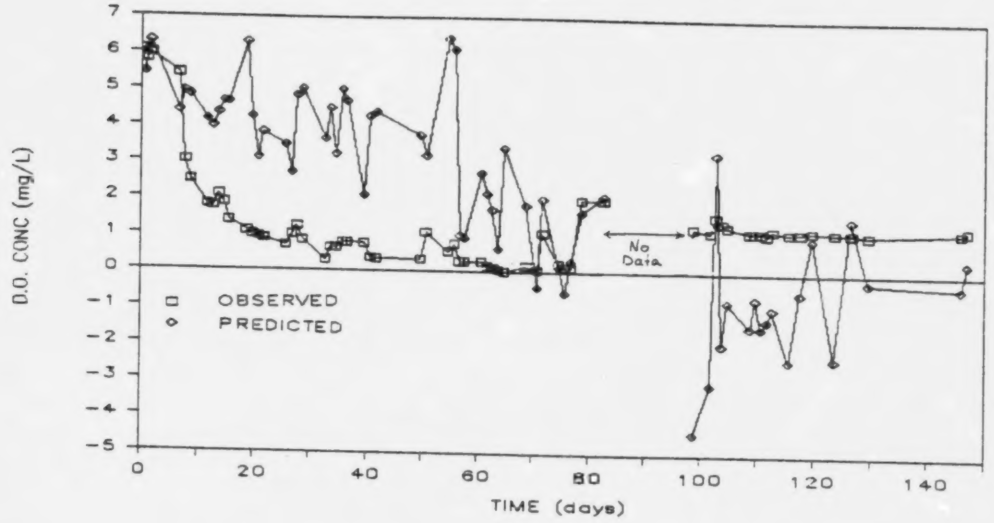


Figure 3.8: Observed and predicted D.O. concentrations in the effluent

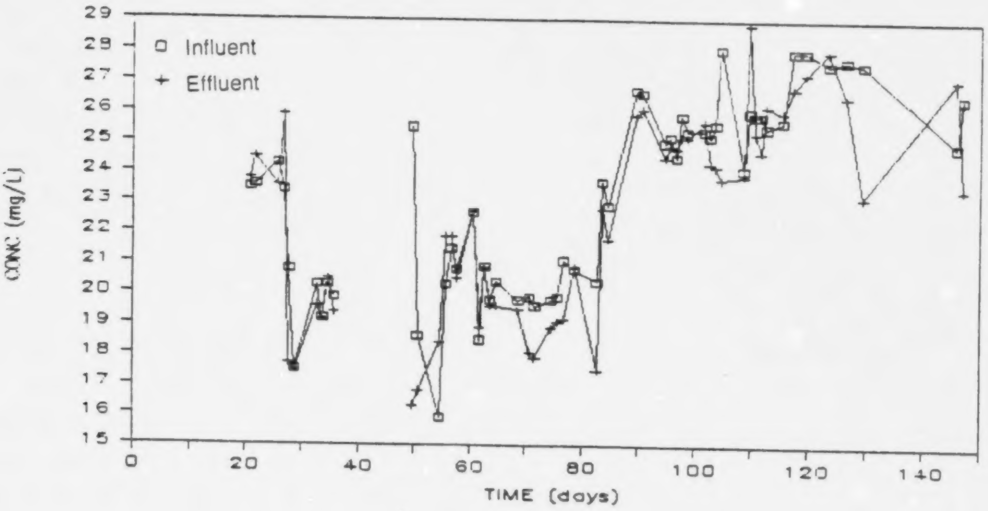


Figure 3.9: Observed NO_3^- concentrations in the influent and effluent solutions.

Potassium nitrate was added on day 21 to the influent to produce a nitrogen concentration of about 21 mg/L and was accidently removed from the influent on day 37. During the 15 day period in which the column received nitrate, no nitrate losses were observed. However, BTEX losses increased to about 40% of the influent.

Nitrate was added to the influent solution again on day 49. With time, the BTEX lost within the column increased (Figure 3.7) perhaps because of bacterial growth.

Figure 3.8 is a plot illustrating observed and predicted D.O. concentrations in the effluent. Predicted D.O. concentrations were calculated using the measured influent D.O. concentration, observed BTEX losses and stoichiometry of toluene mineralization (equation (3)). Observed D.O. concentrations in the effluent decreased to less than 1 mg/L within the first 20 days and remained below 1 mg/L until about day 65. Prior to day 65, the predicted D.O. concentrations were 2 to 3 mg/L greater than observed, indicating that biodegradation of BTEX in the column was insufficient to produce the observed D.O. losses. This result is consistent with the results of microcosm Experiment 4. The additional oxygen loss was previously attributed to biodegradation of non-BTEX organics or chemical oxidation. Nitrate was conservative during this period.

After about 65 days, the effluent D.O. concentration increased slightly to 1 to 2 mg/L. The predicted D.O. concentration was lower than the observed indicating that the BTEX loss was greater than could be accounted for by aerobic biodegradation. BTEX may have been incompletely mineralized resulting in the production of biodegradation intermediary compounds (for example, catechol).

Nitrate losses were apparent after 70 days with average losses about 0.5 mg/L (N) (Figure 3.11(b)). Acetylene (5% by volume) was added to the influent solution on days 119 and 144 in order to confirm the occurrence of denitrification. Nitrous oxide, detected in the effluent solution, was approximately equal to the average loss of nitrate indicating denitrification was the major mechanism causing nitrate losses within the column.

Assuming that the additional BTEX, not accounted for by aerobic degradation, was lost during denitrification, this BTEX loss is of the magnitude expected from a nitrogen loss of 0.5 to 1.0 mg/L. The agreement of this mass balance suggests BTEX was transformed during denitrification. The occurrence of denitrification in the presence of low but detectable D.O. is consistent with the results of the microcosm experiments.

A lag period preceded the onset of nitrate utilization. After the addition of nitrate on day 49, nitrate remained conservative until about day 65, coincident with the the time when BTEX losses became greater than accountable for by aerobic biodegradation only. This lag period of about 15 days, may represent the time necessary for a significant number of denitrifiers to evolve or it may represent the time required for denitrifying enzymes to be induced. The length of the lag period could have been shortened because of the short exposure to nitrate between days 21 and 37.

Figure 3.10: Observed BTEX concentrations along the length of Column 2 (a) day 16 (b) day 146

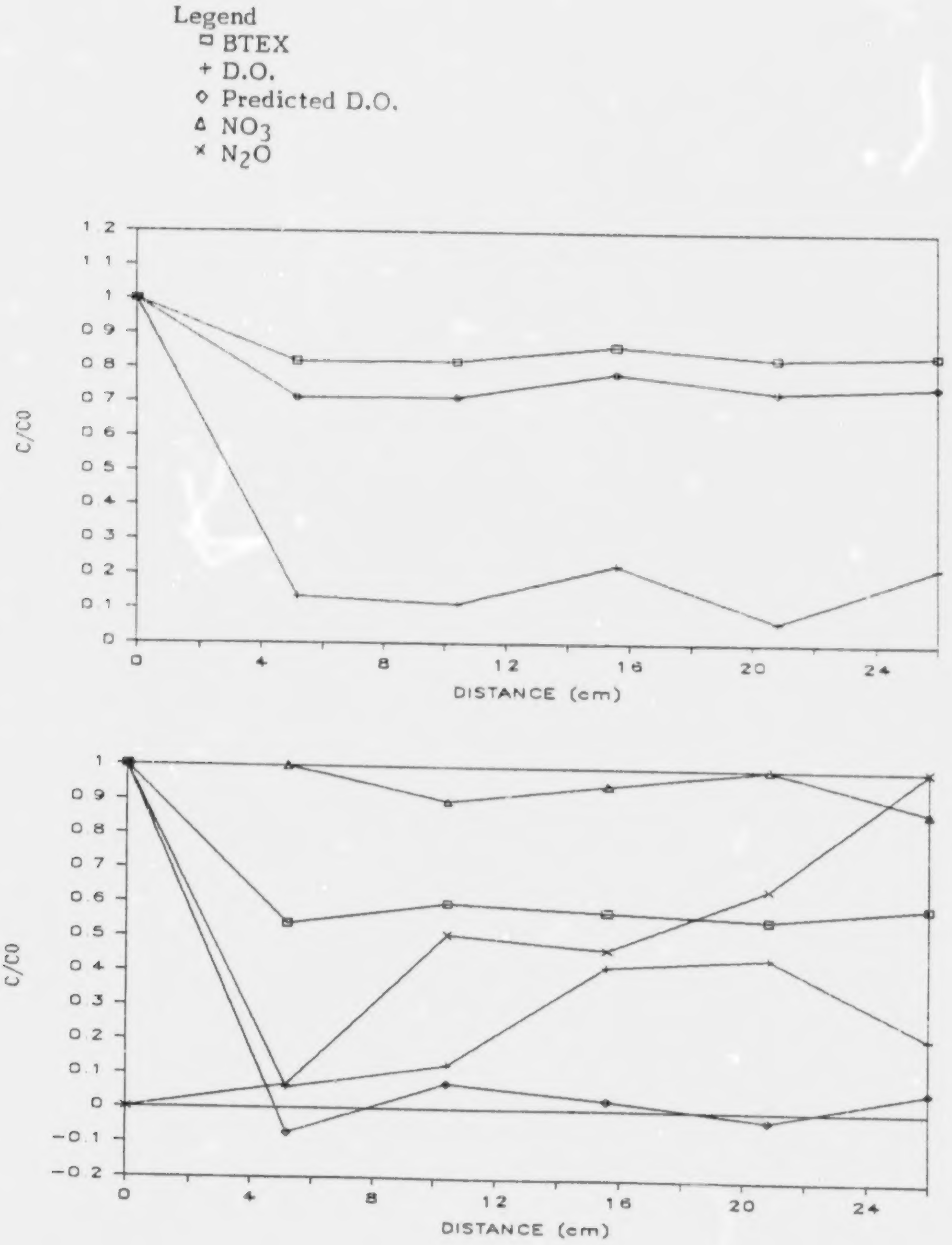


Figure 3.10 is a set of profiles illustrating BTEX, D.O., NO_3^- and N_2O concentrations along the column length during the absence (day 16) and presence (day 146) of nitrate. The profile for day 16 shows a significant reduction of oxygen within the first 5 cm of the column. This loss was greater than predicted from the corresponding BTEX loss for reasons previously discussed. Further reduction of the D.O. concentration to below detection (about 0.02 mg/L) did not occur along the column length indicating that the greatest microbial activity occurred within the first few centimeters of the column. The BTEX concentration was also reduced somewhat in this zone due to biodegradation and/or sorption and further reductions along the column length were insignificant.

The day 146 profile shows both BTEX and D.O. concentrations to be significantly reduced during the first 5 cm of the column. The magnitude of the BTEX loss was greater than expected from sorption and was attributed to biodegradation. The BTEX concentration remained constant throughout the remainder of the column while the D.O. concentration increased somewhat towards the middle perhaps indicating transient conditions, a fluctuating influent concentration or diffusion of oxygen from the column end. The predicted D.O. concentration was less than observed indicating that the BTEX loss at the front of of the column was greater than accountable for by aerobic mineralization. Nitrate concentrations fluctuated throughout the column. Nitrous oxide was detected at a very low concentration at 5 cm and increased towards the end of the column. The nitrous oxide and D.O. distributions indicate an aerobic zone occupied the first 5 cm of the column with the remainder being predominantly denitrifying.

BTEX was not significantly removed within the denitrifying zone but BTEX losses in the aerobic zone exceeded the aerobic capacity of the zone. Perhaps aerobic bacteria initiated the breakdown of BTEX and denitrifiers augmented the breakdown by further transforming the BTEX intermediates during denitrification. Such a degradative process is consistent with Experiment 3 microcosm results using ^{14}C-labelled benzene, where the addition of nitrate to both aerobic and anaerobic microcosms resulted in the more complete mineralization of benzene.

In summary, the results from this column experiment indicate that denitrification can occur in close association with an aerobic environment. BTEX losses when nitrate was present exceeded those from aerobic biodegradation alone. A lag period of about 15 days preceeded the onset of nitrate utilization and because the nitrate lost from the system was converted to nitrous oxide, the lag period may be interpreted as a lag period for denitrification. Distributions of D.O., BTEX, and nitrous oxide within the column suggest that BTEX are not transformed during denitrification but instead, their transformation is enhanced by the combined activity of aerobic and denitrifying bacteria.

3.5 SUMMARY OF LABORATORY STUDIES AND FIELD IMPLICATIONS

BTEX from gasoline were degraded aerobically in microcosms and columns containing Borden groundwater and aquifer material but the oxygen required to do so was greater than the theoretical requirements for mineralization. Comparison of aerobic biodegradation rates obtained for BTEX with BTX biodegradation rates indicates that BTEX degrades more slowly than pure dissolved BTX. Other gasoline components dissolved with BTEX were preferred or alternative substrates for actively degrading bacteria. This implies that, in the field, BTEX should degrade more slowly than BTX did in the previous field experiment (Patrick et al., 1986). The results from the oxygen limited column experiment indicated that BTEX biodegradation should be rapid enough such that BTEX and dissolved oxygen do not occur together in significant concentrations because of the utilization of oxygen during biodegradation.

BTEX were transformed, albeit very slowly, during denitrification under strictly anaerobic conditions. The results from the column experiment indicated that the removal of BTEX was enhanced by a combination of aerobic and denitrifying activity. The apparent enhancement of the aerobic removal of BTEX may not have been due to nitrogen assimilation but instead, due to the co-operative degradative efforts of aerobic and denitrifying bacteria. From these results, it is uncertain what the effect of nitrate addition will be on BTEX persistence in the field experiment. Perhaps when both nitrate and oxygen are present for BTEX biodegradation, removal of BTEX could be very rapid but when nitrate alone is present, BTEX removal may be quite slow.

3.6 THE FIELD EXPERIMENT

A natural gradient injection experiment was conducted within a shallow, sandy aquifer. Two volumes of gasoline-contaminated groundwater containing BTEX were injected below the water table. In situ remediation was attempted by the addition of nitrate upgradient from one BTEX slug. It was anticipated that after oxygen depletion of the BTEX slug because of biodegradation, bacteria would use nitrate as an oxidizing agent and BTEX biodegradation could continue under anaerobic conditions. Comparison of the persistence of BTEX in both unremediated and remediated situations would allow evaluation of nitrate addition as a remedial measure.

3.7 THE BORDEN SITE

The injection experiment was conducted in an unconfined sand aquifer at Canada Forces Base Borden near Barrie, Ontario (Canada). The experimental site is situated in an abandoned sand quarry, 350 m down gradient from an abandoned landfill. The landfill leachate plume has been studied and modelled by researchers at the University of Waterloo (Egboka et al., 1983; MacFarlane et al., 1983;

Nicholson et al., 1983). The site was used during 1984 for the study of the behaviour of dissolved benzene, toluene and xylene isomers (BTX) in groundwater (Patrick et al., 1985). Prior to this, the site was also used for a large-scale tracer study of halogenated organic compounds (Mackay et al., 1986a). This site is also near other tracer sites described by Sutton and Barker (1985) and Sudicky et al. (1985). The Borden site was chosen for this experiment because the hydrogeology is relatively well understood and a monitoring network was already present.

Table 3.6: Chemical Characteristics of the Uncontaminated Groundwater

Paramter		Concentration
Ca^{2+}	mg/L	77
Mg^{2+}	mg/L	4.5
Na^{+}	mg/L	1.7
K^{+}	mg/L	0.15
Fe total	mg/L	0.02
Alkalinity as $CaCO_3$	mg/L	200
Cl^{-}	mg/L	0.7
SO_4^{2-}	mg/L	18
TDS	mg/L	225
DOC	mg/L	0.7$^{(1)}$
TOC	mg/L	7.0
DO	mg/L	0-5.0
NO_3^{-}-N	mg/L	0.10
NO_2^{-}-N	mg/L	n.d.
NH_3^{+}-N	mg/L	n.d.
TKN-N	mg/L	n.d.
Temperature	°C	8-10
pH	---	8.1

(1) Mackay et. al., 1986a
n.d. not detected

The aquifer consists of medium- to fine-grained sand of glaciofluvial origin (MacFarlane et al., 1983) which extends from the ground surface to a depth of about 9 m. Major hydrogeologic properties of the aquifer are listed by Mackay et al. (1986a). The organic carbon and clay mineral content of the sand are very low. The sand exhibits small scale horizontal bedding with an average layer thickness of 0.01 m (Patrick and Barker, 1985) and hydraulic conductivity contrasts as great as two orders of magnitude (Sudicky, 1986). These beds are discontinuous laterally on a scale of 1.0 to 1.5 m. The sand is underlain by a thick and relatively impervious clay till.

The shallow water table occurs at a depth which varies between 0.0 and 1.0 m below ground surface depending upon local precipitation amounts. The previous injection experiments indicated that groundwater velocity was relatively constant at about 0.10 m/day, however the direction varied between north and northeast.

Variation of the magnitude and direction of velocity has been attributed to seasonal water table mounding at the landfill (MacFarlane et al., 1983). During previous summers, vertical hydraulic gradients were minimal at the site and flow was predominantly horizontal.

The lower third of the aquifer is occupied by a leachate plume while the upper two-thirds of the aquifer is unaffected (MacFarlane et al., 1983). The experiment was conducted within the uncontaminated upper zone. The chemistry of the groundwater from the upper zone is presented in Table 3.6. Prior to the onset of this experiment, the aquifer was cored and groundwater sampled in order to confirm that previous field experiments had not contaminated this site.

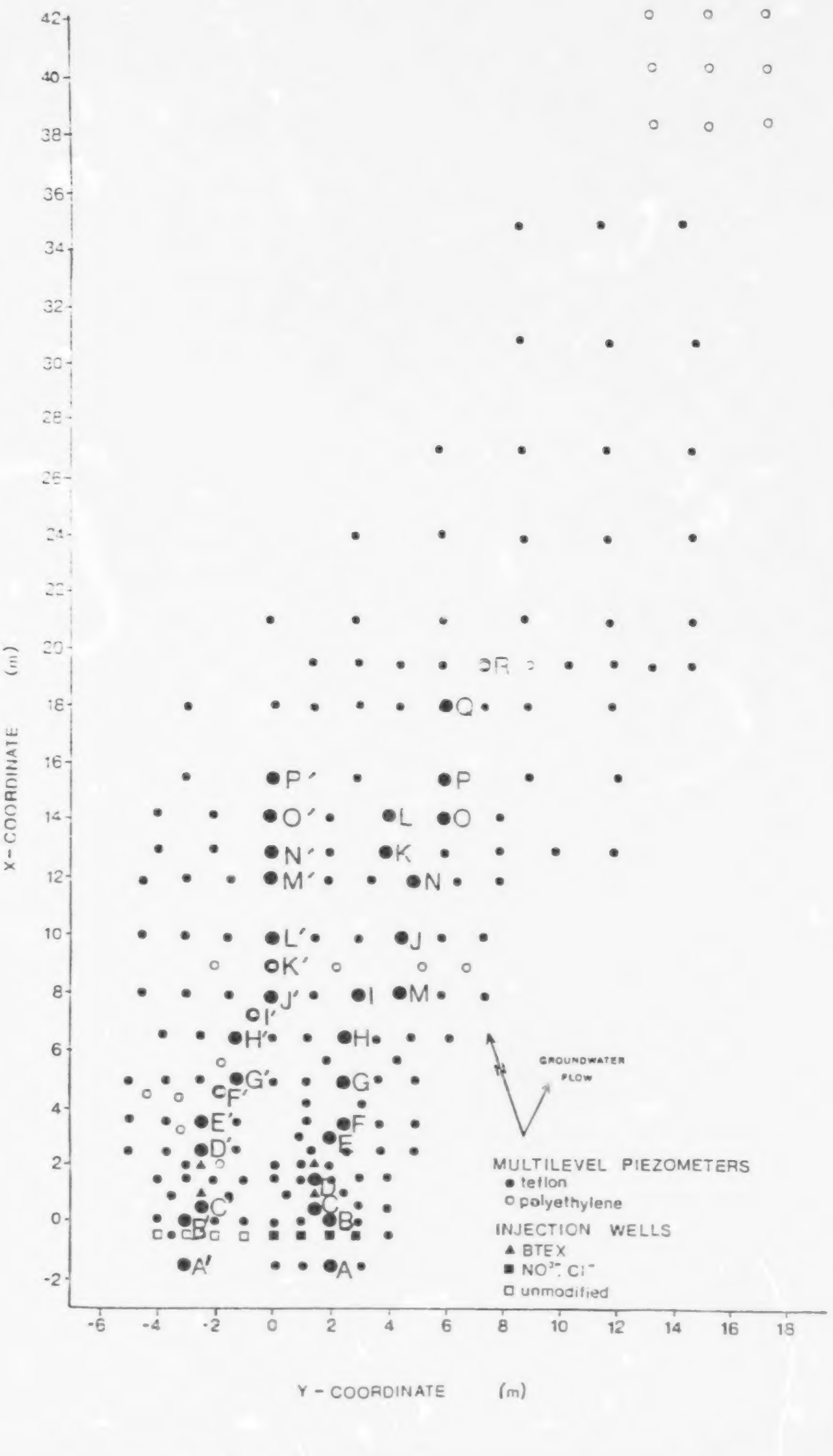
3.8 MONITORING NETWORK

The network consisted of the original teflon bundle piezometers installed for the Stanford University and University of Waterloo experiment (Mackay et al., 1986b), piezometers installed later (Patrick et al., 1985) and piezometers installed for this study. Figure 3.11 is a plan view of the monitoring network for this experiment.

The multilevel piezometers consisted of 12 to 23 3.2 mm O.D. teflon or polyethylene tubes, the ends of which were spaced vertically at 0.20 m or 0.30 m intervals. These piezometers allowed monitoring of the depth interval of approximately 1.8 to 5.4 m below ground surface. The methods employed for installation are described in Appendix A.

During the previous field experiment and accompanying laboratory experiments, it was concluded that BTX could penetrate polyethylene tubing and subsequently desorb into clean water. This led to the detection of BTX in piezometer points below the presumed location of the BTX plume (Patrick, 1986). This was particularly true for concentrations of BTX greater than 1 mg/L. Data obtained from polyethylene piezometers were carefully scrutinized during this field experiment and, because the BTEX concentrations in contact with the polyethylene piezometers were so low, it was concluded that contamination of clean samples by desorption had not occurred.

Figure 3.11: Piezometer and injection well locations at the Borden field site. Letters reference well locations for Figures 3.12, 3.16 and 3.17.


X - COORDINATE (m)
Y - COORDINATE (m)
-6
-4
-2
0
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D
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E
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G'
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I'
I
J'
J
K'
K
L'
L
M'
M
N'
N
O'
O
P'
P
Q
R
N
GROUNDWATER FLOW
MULTILEVEL PIEZOMETERS
● teflon
○ polyethylene
INJECTION WELLS
▲ BTEX
■ NO3⁻, Cl⁻
□ unmodified

3.9 THE FIELD INJECTION

The selection of injection solution volumes, the design of the injection system, and the development of analytical procedures greatly benefitted from experimental design and procedures described by Patrick et al. (1985) and Mackay et al. (1986b). Details of the design and implementation of this field experiment are given in Appendix A.

Two injections took place in June, 1986. Both injections introduced a known volume and concentration of dissolved constituents below the water table. Injection water was obtained from a well screened within the uncontaminated zone of the aquifer and located approximately 150 m north of the site. This water contained dissolved oxygen at a concentration ranging from about 2.5 to about 3.5 mg/L.

The initial injection commenced on June 18, 1986 and introduced two separate water volumes containing BTEX in the form of gasoline-contaminated water into the unconfined sandy aquifer. This was accomplished by a continuous flow system in which a concentrated spike solution of gasoline-contaminated water was mixed and diluted with stored groundwater. The resulting solution was injected under natural gradient conditions by pumping through four injection wells (Figure 3.11) screened over a depth interval of 2.3 to 2.9 m below ground surface. 5000 L was injected (1250 L per well) in 13.9 hours. The injection solution was sampled frequently at the injection wells to estimate the total mass and average concentration of BTEX and dissolved oxygen injected (Table 3.7).

The second injection, on June 22, 1986, introduced a similar volume of water containing nitrate and chloride ions. Since nitrate is known to be involved in many biological processes, chloride was added as a conservative tracer to follow the potential nitrate migration. Again, a continuous flow system was used and the resulting injection solution was injected through four injection wells upgradient from the 2 eastern BTEX injection wells (Figure 3.11). Four similar injection wells, upgradient from the two western BTEX injection wells, received unmodified groundwater so that both BTEX slugs received identical hydraulic treatment. The injection wells for water containing nitrate and unmodified groundwater were screened over a depth interval of 2.0 to 3.6 m below the ground surface. This injection continued for 13.3 hours. A total of 4800 L was injected through eight wells although only 2400 L contained added nitrate and chloride. The mass of chloride and nitrate added was determined by weighing the potassium nitrate and sodium chloride prior to spike solution preparation. Samples of the injection solutions were obtained to determine the average oxygen, nitrate and chloride concentrations.

Table 3.7 lists the initial masses and average concentrations for the organic and inorganic solutes. The BTEX concentration of the spike solution was lower than desired because the gasoline used for the field experiment was different from the gasoline used during laboratory callibration of the equipment. BTEX losses also occurred within the injection equipment after addition of the spike solution and are attributed to sorption. Losses due to volatilization were assumed minimal since the injection system was sealed to prevent losses however, some volatile losses may have occurred within the injection well stand pipes.

Table 3.7: Estimated Amounts of Solutes Injected

Solute	Estimated Mass	Average Injection Concentration
Gasoline Contaminated Water(1)		
Benzene	0.252 g	0.101 mg/L
Toluene	0.675 g	0.270 mg/L
Ethyl Benzene	0.192 g	0.077 mg/L
P-Xylene	0.203 g	0.081 mg/L
M-Xylene	0.549 g	0.220 mg/L
O-Xylene	0.322 g	0.129 mg/L
Total BTEX	2.193 g	0.878 mg/L
Dissolved Oxygen	5.75 g	2.3 mg/L
Remedial Injection		
Chloride	4.8 kg	2000 mg/L
Nitrate	107.8 g	44.9 mg/L
Dissolved Oxygen	8.4 g	3.5 mg/L

(1) amounts reported for 1 slug (2500 L) only

3.10 SAMPLING PROCEDURES

The primary objective of the field sampling program was to obtain synoptic data or "snapshots" of the three-dimensional distribution of concentrations at approximately monthly intervals. A complete set of BTEX, nitrate, chloride, and dissolved oxygen samples sufficient for one snapshot were typically recovered within three days. Multilevel piezometers were sampled with a sampling vacuum manifold modified from the original design described by Mackay et al. (1986b). The use of a sampling manifold enabled simultaneous sampling of fourteen piezometer points with simultaneous collection of one sample for BTEX analysis and one sample for inorganic analyses per sampling point. Water was drawn from a piezometer tube into an 18 cm^3 glass hypovial (BTEX sample) and overflow from this was collected in a 20 cm^3 vial (inorganic sample). An additional 50 cm^3 of overflow was collected in an erlenmeyer flask to ensure adequate flushing of the piezometer tube. The inorganic sample was split after collection to provide separate water volumes for chloride and nitrate analyses. Water samples for D.O. measurement were collected prior to sampling with the vacuum manifold. Separate samples for BTEX, chloride, nitrate, and dissolved oxygen analyses were obtained in order to preserve each sample type appropriatly and to avoid analytical interferences. All samples, except those for D.O. measurement, were stored in coolers with cold packs, transported to the University of Waterloo and stored at $4^{0}C$ prior to analysis. The manifold was designed such that sample water contacted only teflon, brass, and glass. Samples for BTEX analyses were open to the atmosphere for less than five seconds while being poisoned with 0.2 cm^3 of 10% sodium azide solution and sealed with teflon-faced silica septa. The hypovials were completely filled leaving no entrapped air. Patrick (1986) concluded from a sampling study using the vacuum manifold that sampling techniques introduced a bias of about -5% for BTX due to sorption and volatilization.

Samples for chloride and nitrate analyses were stored in 20 cm^3 polyethylene bottles. Sample water for nitrate analysis was preserved by acidifying with 1 drop of concentrated sulphuric acid. The sample bottles were shaken to aerate the water in hope that oxygen would further inhibit nitrate losses through denitrification.

Dissolved oxygen measurements were made on 50 cm^3 samples obtained from selected points at piezometers along transects both perpendicular and parallel to the BTEX slugs. A peristaltic pump was connected to the piezometer tube to be sampled using a plastic tubing adapter and a small piece of silicon tubing. Water from the piezometer point was collected using another adapter fitted to the neck of a 50 cm^3 ground glass syringe allowing collection of the groundwater without exposure to the atmosphere. The syringe was flushed once before sample collection to remove oxygen from the syringe and to flush the piezometer tube. All measurements were made in the field, using the Winkler method with azide modification using the 50 cm^3 glass syringes as reaction vessels. Details of this method are described in Appendix B.

For each sampling session, only a portion of the total network was sampled. From the total number of samples collected and the initial solute concentrations, it was estimated that sampling the experimental slugs resulted in the total removal of less than 2% of the BTEX and 5% of the chloride and nitrate initial masses. Based on estimated solute velocities, an attempt was made, during each sampling session, to sample the gasoline and nitrate/chloride slugs completely. However, sampling sessions in October and November (days 113 and 148) did not sample the entire chloride/nitrate slug, resulting in up to 20% error in the calculation of mass.

3.11 DATA MANAGEMENT AND ANALYSIS

Five snapshot sampling sessions were completed resulting in the collection of thousands of samples which were analyzed for BTEX, chloride and nitrate. In addition, over 500 Winkler titrations were performed to measure dissolved oxygen. The large data set necessitated implementation of computer assisted manipulations. Snapshot data sets were treated in a manner similar to that described by Patrick (1986) in order to estimate the total mass, concentration distribution, and velocity of each solute.

All snapshot data, excluding oxygen data, were entered into computer data files. Background concentration values were then subtracted from the sample analyses and subsequent sample values were adjusted according to the error in the analyses of laboratory controls. To reduce the complexity of illustrating the experiment in three dimensions, each data set was then reduced to two dimensions by using trapezoidal quadrature (Hornbeck, 1975) to integrate the concentration versus depth function at each multilevel piezometer. This manipulation yielded a number representative of the mass of a solute at a piezometer location. The integrated concentration values and the x,y co-ordinates of the corresponding piezometers were then entered into the Surface II computer graphics routine (Sampson, 1978) to obtain two-dimensional (horizontal) contour plots of each solute. Surface II is a software package which interpolates the initial iregularly spaced two-dimensional data to a regular, dense grid. Patrick (1986) defined the optimum grid spacing and interpolation options for the Borden site and these were used in the interpolation routine applied in this study.

The point solute concentration distribution was subjected to spatial moment analysis. The zeroth and first moments represent the mass and location of a solute plume, respectively. Moment estimates were made using the dense grid generated during the Surface II routine. This method is described by Freyburg (1986).

An analysis of error introduced by the interpolation routine indicated increasing positive error in mass estimation for decreasing sampling grid density for an analytically generated point source contaminant slug (Bumbalis et al., 1987). For a grid density to BTX plume or slug length ratio of 0.8 (characteristic of the field experiment conditions at very late times), the error in mass estimation could be about +180%. The error in calculation of centre of mass was considerably less and was found not to exceed 5%.

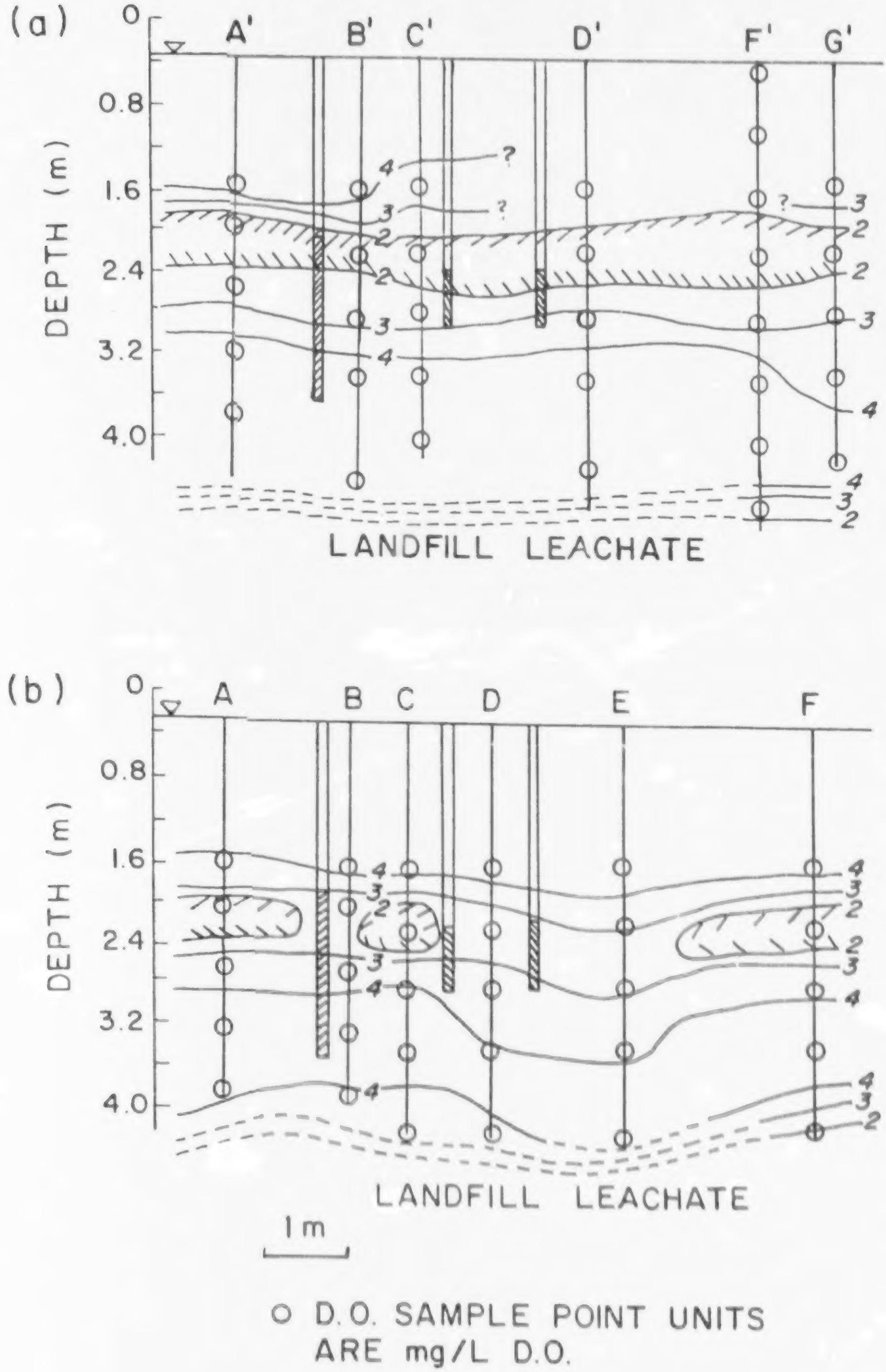
3.12 RESULTS OF THE FIELD EXPERIMENT

Discreet three dimensional solute distributions or "snapshots" were taken 8, 30, 78, 113 and 148 days after the initial injection. This data was used to assess both the horizontal and vertical distribution of the organic and inorganic solutes. Velocity and mass estimates were made to determine biodegradation and mobility of the gasoline-derived BTEX and the affect of nitrate addition as an in situ remedial measure. Results presented herein are quite complex because of the heterogeneous nature of the Borden aquifer. Interpretation of the results tends to be speculative.

3.12.1 Pre-injection Conditions

The pre-injection distribution of dissolved oxygen was determined 24 hours prior to injection. The vertical distribution of D.O. in the vicinity of the injection wells was dominated by layering centred around a band of water containing D.O. concentrations of less than 2.0 mg/L (Figure 3.12). This band was approximately 5 m thick and occurred at the same depth interval as the gasoline-contaminated water injection well screens. A similar banded D.O. distribution existed at this site, two years prior to this experiment, and is described by Patrick et al. (1986). The reason for this low D.O. zone is unclear but results from microcosm experiments using groundwater and aquifer material from this zone suggested that the solid organic matter may have been utilizable by bacteria during aerobic biodegradation and denitrification. Perhaps this zone contained more favourable organics for bacterial degradation than other parts of the aquifer.

Figure 3.12: Pre-injection distribution of dissolved oxygen (piezometer locations are shown in Figure 3.11)


(a)
A'
B'
C'
D'
F'
G'
DEPTH (m)
0
0.8
1.6
2.4
3.2
4.0
4
3
2
?
LANDFILL LEACHATE
(b)
A
B
C
D
E
F
1 m
○ D.O. SAMPLE POINT UNITS ARE mg/L D.O.

3.12.2 Solute Distributions

Two-dimensional, horizontal illustrations of the distribution of chloride and nitrate are presented in Figure 3.13 and of benzene, toluene, and m-xylene are shown in Figure 3.14. Shown are depth-integrated concentrations which were contoured using the Surface II graphics program (Sampson, 1978). On day 8, both unremediated and remediated aromatic slugs exhibit a circular distribution (Figure 3.14) and the chloride and nitrate distributions were ovoid as expected from the injection well geometry. Concentration gradients for all solutes were sharp, indicating dilution due to dispersion was insignificant within the first eight days of the experiment. In cross-section, unremediated and remediated benzene and nitrate assumed irregular shapes (Figure 3.16 - day 8). Similar initial conditions also existed for previous injection experiments conducted at the Borden site (Patrick et al., 1986; Mackay et al., 1986b; Sudicky et al., 1985) and have been attributed to hydraulic conductivity contrasts or "heterogeneities" in the form of layers. The irregular nature of the initial BTEX conditions of this study may also be in part due to variation in the injection water composition (Appendix A).

Figure 3.13 shows similar distributions of chloride and nitrate at all snapshot times. Nitrate and chloride also show identical vertical distributions in Figure 3.15, a time series of profiles at a single piezometer. If nitrate was used in biological reactions, such utilization was not recognized by its distribution.

With time, the nitrate and chloride slugs became elongated in the direction of flow (Figure 3.13) and after 148 days, had spread to a length of over five times the initial slug length. Little spreading had occurred in either the vertical or horizontal directions transverse to flow (Figures 3.13 and 3.16). These observations of longitudinal and transverse dispersion are consistent with previous observations of dispersion at Borden (Sudicky et al., 1983; Mackay et al., 1985b; Patrick et al., 1986). This suggests that the dominant mixing process is longitudinal dispersion while transverse dispersion is a relatively weak process, on the order of molecular diffusion (Sudicky, 1986).

Several of the organic solutes also show some elongation in the direction of flow but it is much less than that shown by the inorganic solutes (Figure 3.14). Maximum dispersion is shown by benzene, which elongated to only twice its original length by day 78. Within 148 days, each organic solute slug had undergone a reduction in size which may or may not have been preceeded by some elongation. The decrease in slug size is attributed to mass loss and is believed to be the result of biodegradation since sorption is reversible and BTEX are not believed to partake in any chemical reactions (Patrick et al., 1985).

Overlap of nitrate and benzene, in plan view, increased with time and by day 148, the nitrate slug began to appear down gradient from the benzene slug (Figure 3.14). Overlap of the other remediated compounds was less well developed because they disappeared almost completely before the overlap was complete. Solute transport was such that, with a minimum of hydraulic control, nitrate was mixed with existing gasoline-contaminated groundwater under natural hydraulic gradients.

Figure 3.13: Contour plots of vertically averaged concentrations showing chloride and nitrate at 8, 30, 78, 113 and 148 days after injection

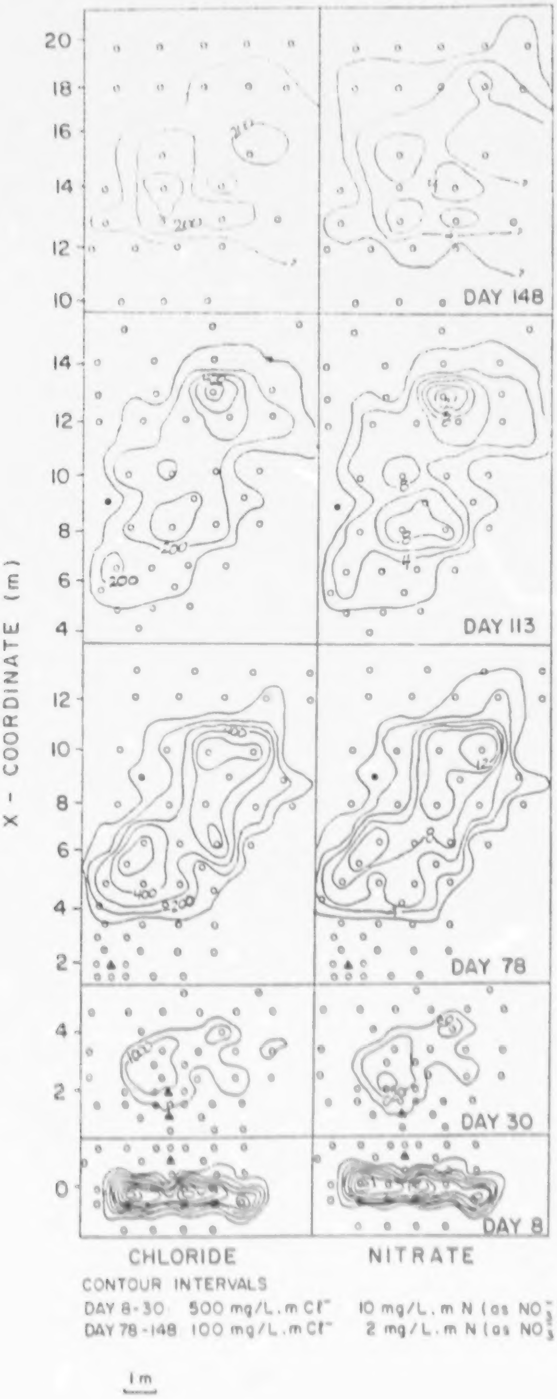
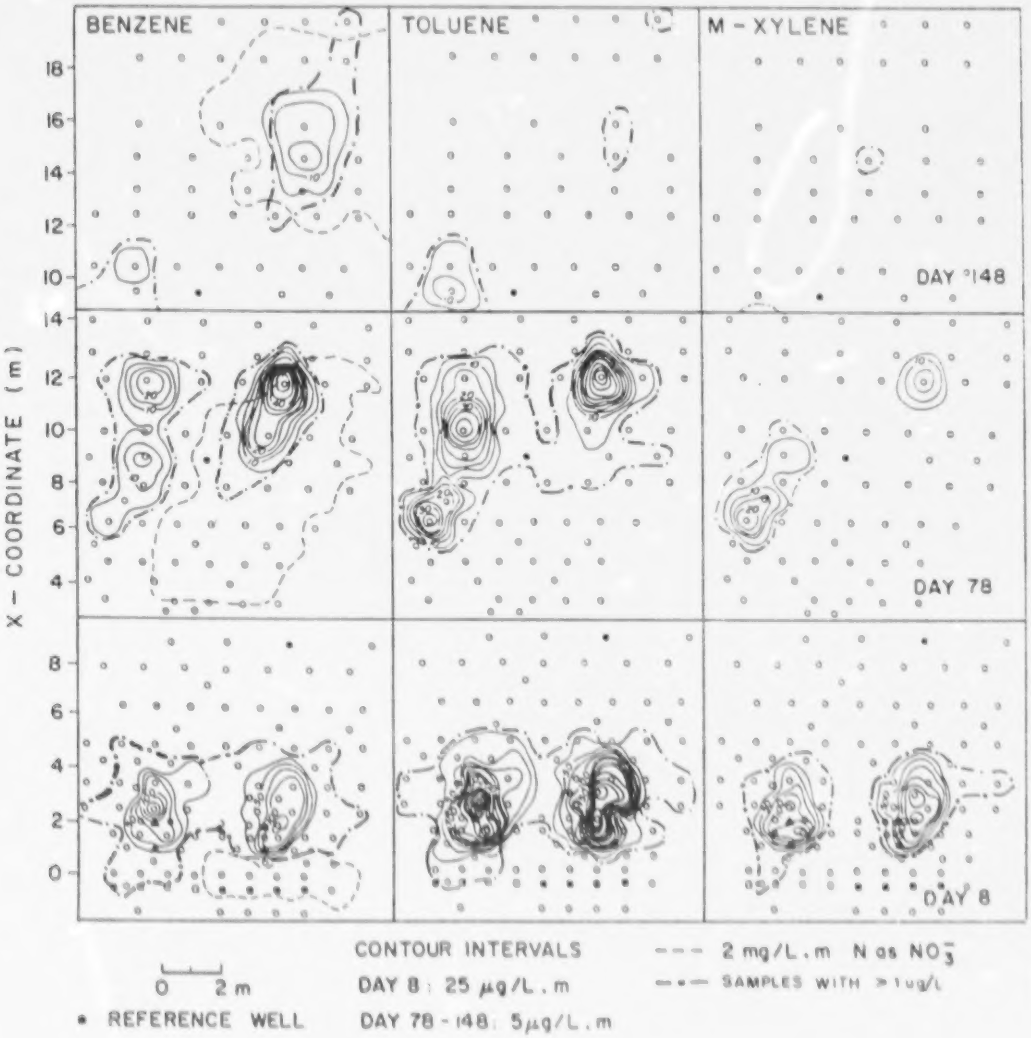


Figure 3.14: Contour plots of vertically averaged concentrations showing toluene, benzene, and m-xylene at 8, 78, and 148 days after injection



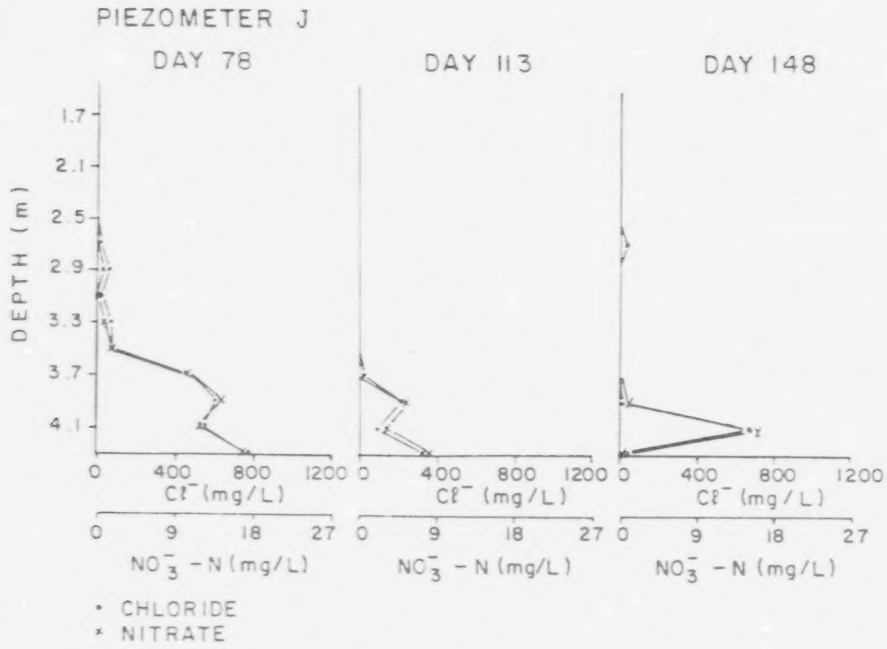


Figure 3.15: Nitrate and chloride concentration - depth profiles at a multilevel piezometer. (piezometer location is shown in Figure 3.11)

Comparison of the D.O. contours on day 8 (Figure 3.16) with those of the pre-injection profiles (Figure 3.12) indicates a disturbance of the natural D.O. distribution. Although both gasoline-contaminated slugs contained dissolved oxygen at a concentration of about 2.3 mg/L at the time of the injection, the dissolved oxygen content of the slugs was reduced by day 8, thus creating a low D.O. anomoly.

Upgradient from the benzene slugs, the D.O. profiles show oxygen concentrations to be in excess of background. This anomoly is due to the presence of groundwater from the later injection. The D.O. content of the water injected upgradient remained unchanged from the injection concentration of 3.5 mg/L, indicating the decrease in D.O. in the benzene slugs must have involved the presence of organics. It is assumed that the oxygen decrease within the benzene slugs indicates the onset of biodegradation.

Of particular note are the lobate distributions or layering of the solutes when examined in vertical section (Figures 3.16 and 3.17). Benzene, toluene, and m-xylene tended to occupy the same layers and nitrate tended to advect most quickly in these layers. It is assumed that these layers are of higher hydraulic conductivity. The most advanced upper organic lobes correlate with the zone of low dissolved oxygen concentration that was observed prior to injection (Figure 3.12). The lower, generally less advanced organic lobes, progressed towards a well oxygenated zone. This lower lobe contained lower BTEX concentrations than the upper lobe. Patrick et al. (1986) observed a similar lobate distribution of BTX in zones of low and high D.O.

With time, the horizontal and vertical distributions of BTEX became irregular due to the incomplete sampling of the slugs afforded by a sparse monitoring network and decreased slug size. Such behaviour is consistent with observations of BTX distributions at late times (Patrick et al., 1986).

Figure 3.18 is a set of time dependant profiles showing benzene and D.O. concentrations at two piezometers, G and G'. The first two curves in the time series represent the natural fluctuation of D.O. concentrations through the water column. The third set of curves show a more extensive zone with low D.O. due to the presence of benzene. Following removal of benzene, the D.O. levels returned to natural levels.

Although the distributions of the unremediated and remediated organic solutes exhibit many similarities, comparison of their distributions indicates that the unremediated compounds show more longitudinal dispersion than do their respective remediated compounds (Figure 3.14). This is especially apparent for toluene and m-xylene. The unremediated slug in Figure 3.14 developed a bimodal distribution by day 78 which was not developed by the remediated slug. Examination of the slugs in cross-section (Figures 3.16 and 3.17) indicates that the unremediated slug occupies two aquifer layers with BTEX in the upper layer significantly displaced forward of that in the lower. A similar bimodal concentration distribution was observed during a previous conservative tracer test at Borden and was attributed to the influence of two aquifer zones with distinctively different migration rates (Sudicky et al., 1983). Although remediated benzene also occupies two layers, neither solute lobe is significantly displaced forward of the other. Although aquifer heterogeneities in the form of hydraulic conductivity or sorptive properties contrasts may have contributed to the development of differing distributions of the two BTEX slugs, biodegradation may also influence their distributions. The affect of biodegradation on BTEX distribution is discussed in Section 3.14.2 of this report.

Figure 3.16: Contours of benzene, nitrate, and dissolved oxygen distributions along vertical sections (piezometer locations shown in Figure 3.11)

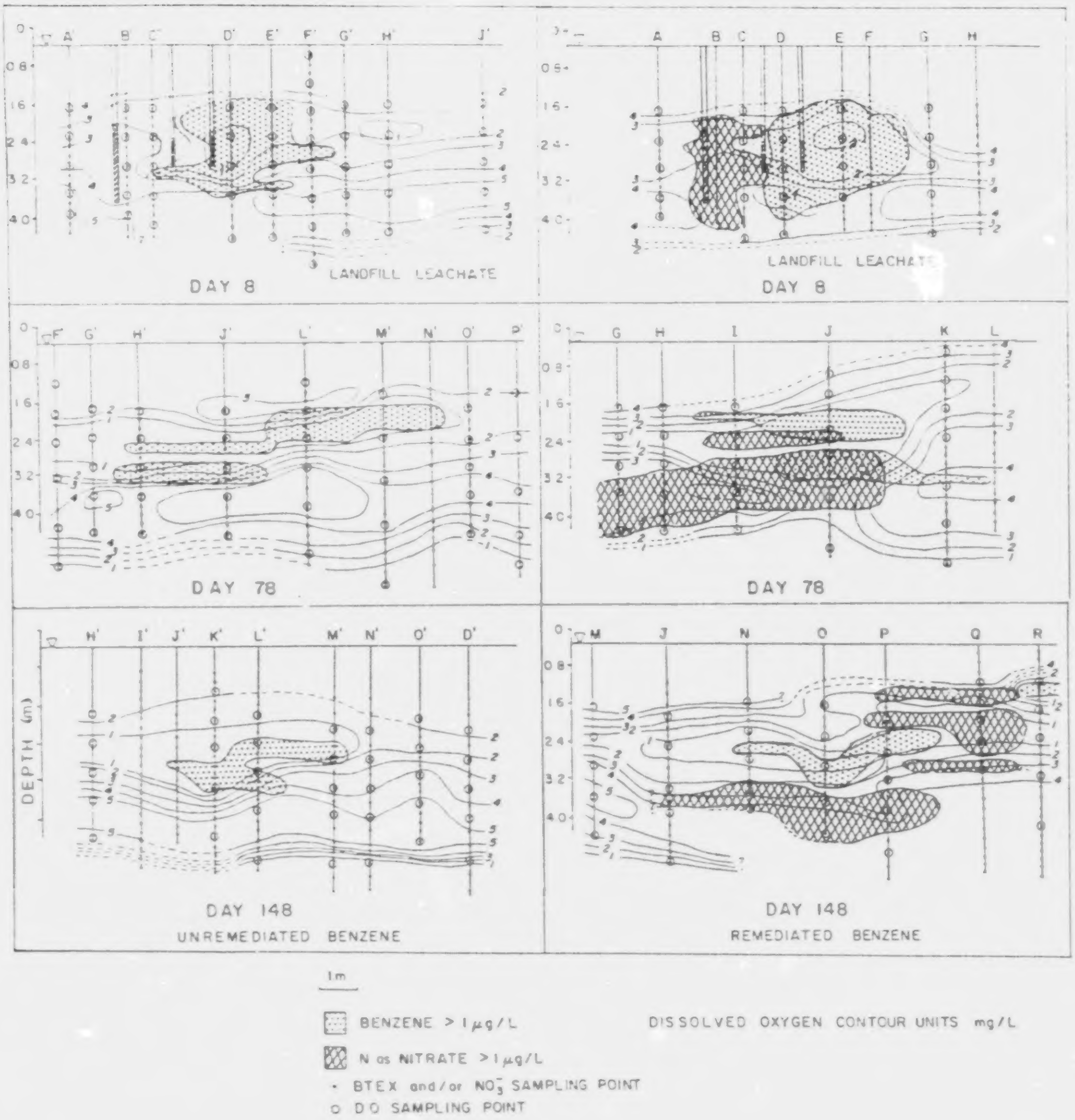
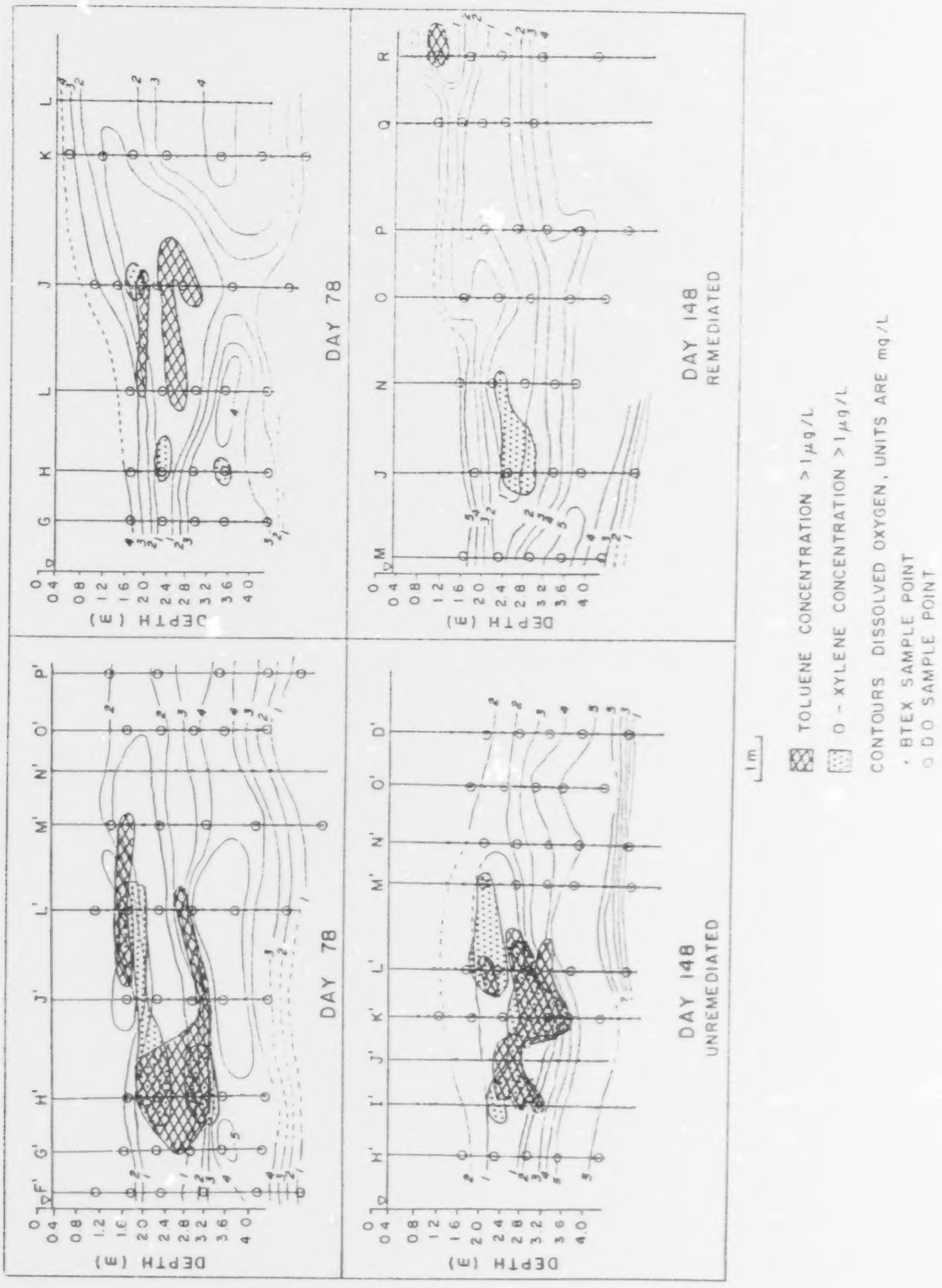


Figure 3.17: Contours of toluene, o-xylene and dissolved oxygen distributions along vertical sections (piezometer locations shown in Figure 3.11)



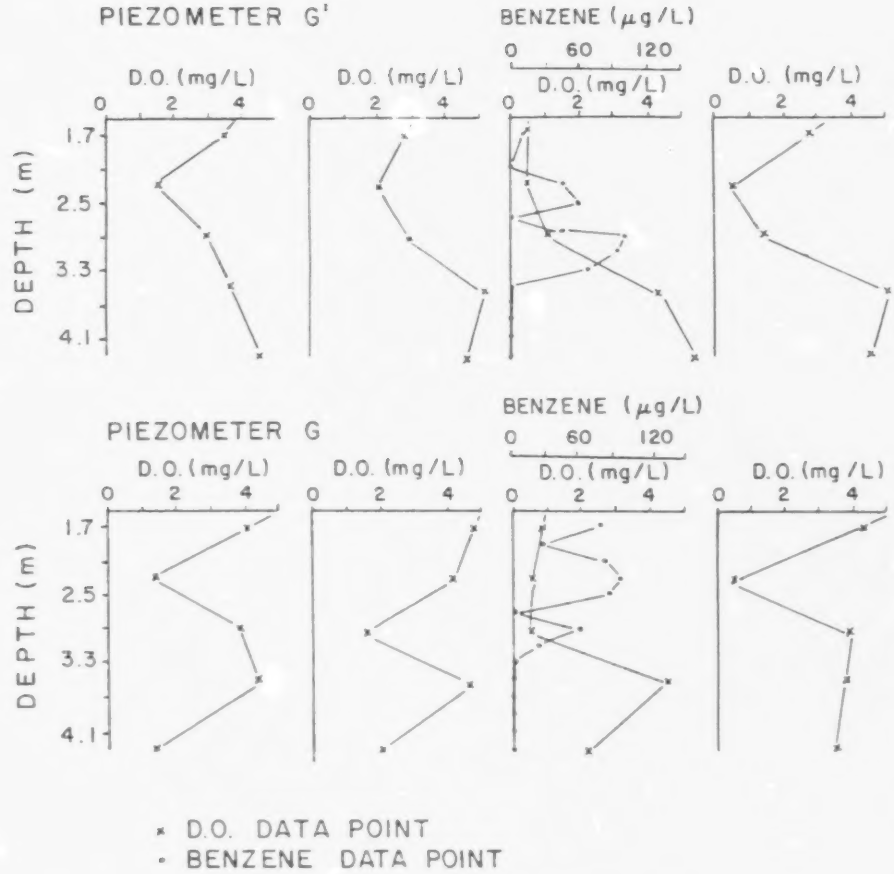


Figure 3.18: Benzene and D.O. concentration-depth profiles at multilievel piezometers (piezometer locations are shown in Figure 3.11)

3.13 VELOCITY AND RETARDATION

Figure 3.19 is a plot of the locations of centres of mass and trajectories for BTEX, chloride and nitrate for the five sampling snapshots. The direction of travel remained constant to the northeast for the duration of the experiment. All three trajectories shown are parallel indicating that neither biodegradation nor sorption of the gasoline constituents influenced the direction of travel.

Groundwater velocity was determined from the positions of centre of chloride mass and was found to have varied from 0.09 to 0.14 m/day through the experiment with an average of 0.11 m/day (Table 3.8).

Figure 3.19: Trajectories of the centres of mass of the solutes

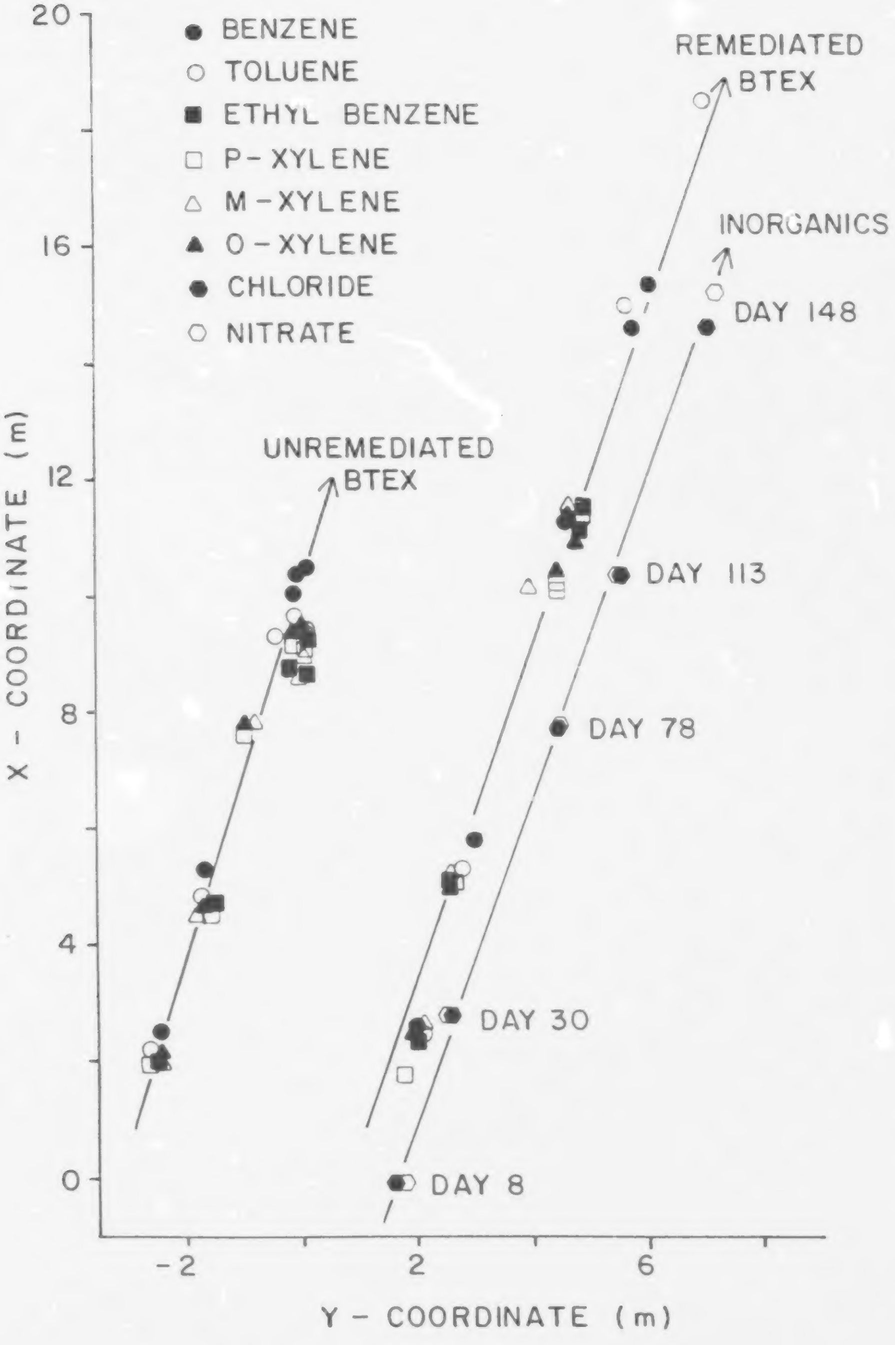


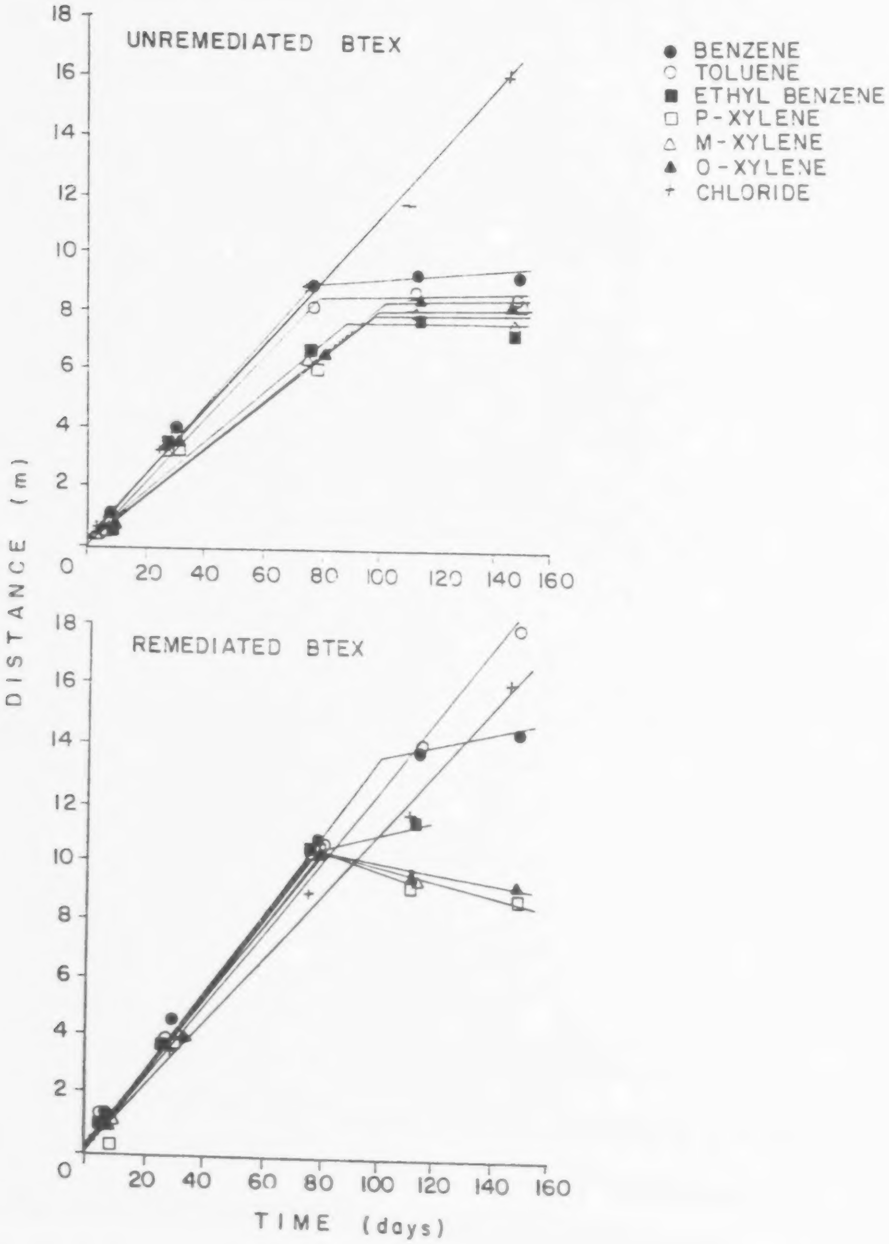
Table 3.8: Velocities Calculated from Centres of Mass

Solute	Velocity (m/d) for Time Period				
	3-8	8-30	30-78	78-114	114-148
chloride	.11	.14	.10	.09	.12
nitrate	.13	.14	.11	.09	.13
UNREMEDIATED					
benzene	.13	.13	.10	.01	.00
toluene	.09	.13	.10	.01	.01
ethyl benzene	.08	.13	.07	.04	.02
p-xylene	.06	.12	.06	.06	.00
m-xylene	.08	.12	.07	.04	.01
o-xylene	.08	.12	.07	.05	.00
REMEDIATED					
benzene	.16	.15	.12	.10	.02
toluene	.14	.13	.14	.10	.11
ethyl benzene	.13	.12	.13	.03	N.D.
p-xylene	.04	.15	.14	.04	N.D.
m-xylene	.14	.12	.14	.04	N.D.
o-xylene	.13	.12	.14	.02	.01

N.D. not determined

Figures 3.20 (a) and (b) are plots of distance travelled with time as determined from centre of BTEX mass locations. Remediated ethyl benzene, p- and m-xylenes were found in only two samples on day 148 so reliable moment estimates could not be made. BTEX data in both figures plot along straight lines, similar in slope to that of chloride, until day 78. A slope reduction then occurred in most of these lines indicating an apparent decrease in velocity of the centres of mass. Velocity decreases were not observed in the previous field injection experiment (Patrick et al., 1986), however, monitoring of the previous experiment was concluded after 108 days and such a phenomenon may have gone undetected. The apparent velocity decreases must be due to biodegradation, sorptive retardation or the effect of aquifer hydraulic conductivity contrasts. Further discussion on this aspect is provided in section 3.13.2.

Figure 3.20: Location of centres of mass with time (a) unremediated BTEX and chloride (b) Remediated BTEX and chloride



3.13.1 Velocity Data Prior to Day 78

Slopes of the regression lines, or velocities, for BTEX were compared to the chloride velocity to determine organic retardation factors. It should be cautioned that chloride occupied a different portion of the aquifer than unremediated BTEX did, so comparison of their velocities may yield somewhat erroneous retardation factors. In addition, with time, both BTEX slugs became smaller so their movement was controlled by the relatively few aquifer layers they occupied. Conversely, the chloride slug expanded with time and its movement represents the average of a much larger volume of aquifer. Nevertheless, bearing in mind these sources of error, the following discussion on retardation is presented.

Regression lines calculated for unremediated BTEX, prior to day 78, plot close to or below the chloride line (Figure 3.20(a)) indicating velocities equal to or less than that of chloride. Unremediated BTEX velocities for individual time periods in Table 3.8 are less than or equal to chloride velocities. This relationship was expected and may be attributed to sorptive retardation. Table 3.9 lists the BTEX retardation factors calculated from the regression velocities prior to day 78. The order of retardations agrees with the order predicted by theoretical calculation (Lymen et al., 1982) and retardation factor values are within the range reported from small scale laboratory experiments by Patrick et al. (1985). In addition, the strong agreement between these retardation factors and those reported for BTX from the Phase II field experiment (Patrick et al., 1986) suggests that the presence of other gasoline-derived organic compounds at the concentrations used in this field experiment did not interfere with sorption processes.

The agreement of field-derived and theoretical retardation factors also implies that biodegradation of unremediated BTEX did not interfere with the sorption processes. For this to occur, mass loss must have occurred uniformly throughout the slug, around the perimeter or at both the front and rear.

Table 3.9: Retardation Factors for BTEX

COMPOUND	UNREMEDIATED	REMEDIATED
Benzene	1.0	0.8
Toluene	1.1	0.9
Ethyl Benzene	1.3	0.9
P-xylene	1.5	1.0
M-xylene	1.5	0.8
O-xylene	1.5	0.8

Remediated BTEX velocities do not follow the retardation trend shown by the unremediated compounds. BTEX regression lines plot above the chloride line (Figure 3.20(b)) and individual time period velocities were greater than chloride's (Table 3.8) indicating centre of mass movement faster than chloride.

Remediated organics may have migrated in layers of higher hydraulic conductivity than those occupied by chloride. The calculated retardation factors would then be expected to follow the same trend as unremediated BTEX with benzene being the most and xylenes being the least mobile. Retardation factors for remediated BTEX are listed in Table 3.9. The rank of least to most mobile remediated organics differs from the unremediated organics indicating advective transport in different aquifer layers was not solely responsible for the velocity trends.

The difference in the remediated and unremediated BTEX retardations may have been due to differing biodegradation processes attributed to the presence of nitrate. Although the remediated compounds may actually have migrated at velocities similar to the unremediated compounds, an enhanced mass removal at the rear of the remediated slug could cause a forward shift in the centre of mass. The occurrence of both nitrate and oxygen at the rear of the remediated slug could enhance both aerobic and anaerobic mass removal.

3.13.2 Velocity Data After Day 78

The unremediated BTEX centres of mass apparently stopped advecting after day 78 (Figure 3.20(a)). As described in section 3.13, the velocity decreases may be attributed to biodegradation, sorption, or hydraulic conductivity contrasts. Gradual velocity decreases with time were observed during the chlorinated hydrocarbons tracer study at the Borden site and were attributed to slow rates of attaining sorption equilibrium (Roberts et al., 1986). Patrick et al. (1985) found sorption of BTX to be consistent with equilibrium reaction processes at groundwater velocities similar to those of the Borden aquifer. This evidence, together with the sudden, as opposed to gradual, velocity changes in Figure 3.20 indicates that the cause of the velocity decreases was not sorption in this case. The BTEX slugs may have encountered less permeable aquifer layers after 78 days, thus slowing their velocity. It seems unlikely that both BTEX slugs would encounter such layers at the same time since the aquifer layers are generally discontinuous laterally on a scale of 1.0 to 1.5 m. In addition, remediated toluene did not slow and remediated benzene slowed later than remediated xylenes suggesting that aquifer heterogeneities were not solely responsible for the velocity cessation.

Biodegradation could have caused the BTEX centres of mass to stop advecting if mass removal was greater at the slug front then at the rear. Figures 3.16 and 3.17 show a zone of water with very low D.O. concentrations behind the unremediated BTEX slug after 78 days. This means that oxygen was unavailable to advect past or mix with the retarded organic compounds at the slug rear thus limiting biodegradation at the slug rear. Water in front of the slug contained higher D.O. concentrations and biodegradation would have been greatest at the slug front as water containing BTEX mixed with the aerobic water by dispersion.

The occurrence of an extensive low D.O. zone behind the BTEX slug may be attributed to the presence of other organics. Many non-BTEX dissolved gasoline components would migrate at velocities less than that of BTEX (for example, napthalene or trimethyl benzene). After 78 days, a noticeable separation of BTEX centres of mass developed due to the different retardations so it may be assumed that some of the non-BTEX aromatics would also separate and lag behind the BTEX slug. Oxygen overtaking the plume could be utilized in the biodegradation of the most retarded compounds first. This would result in minimal oxygen entering the BTEX slug from the rear. The major mechanism for mass removal would then be dispersive mixing and biodegradation at the slug front.

All remediated centres of mass, except toluene, slowed after 78 days. If biodegradation and oxygen limitation caused the cessation, the biodegradation processes must have differed from those affecting the unremediated BTEX slug because the cessation of movement was not simultaneous for all remediated compounds.

Figure 3.16 shows a zone of low D.O. concentrations behind the remediated benzene slug on days 78 and 148, however, this zone was much thinner and less extensive than that behind unremediated benzene. This thin zone limited only the biodegradation of the xylenes from the rear, and so may have resulted in their apparent velocity decreases. Benzene and toluene centres of mass did not slow after day 78 probably because they were still present in zones other than the low D.O. zone and oxygen was present for biodegradation at the rear. By day 113, benzene's centre of mass apparently slowed because oxygen at its rear was utilized in the degradation of xylenes and ethyl benzene. Toluene was unaffected by the oxygen limitation since it was still present in a layer other than the low D.O. zone. The centre of toluene mass continued to move ahead faster than groundwater velocity.

The difference in remediated and unremediated centres of mass behaviour appears to have occurred because of the differing size and extent of the low D.O. zone located behind the slugs. The zone behind remediated BTEX may be less extensive than that behind unremediated BTEX because of the presence of nitrate or aquifer heterogeneities. Perhaps nitrate assisted in the removal of lagging non-BTEX compounds, the biodegradation of which was suggested as a cause for the presence of a low D.O. zone behind unremediated BTEX. Alternatively, perhaps dispersion in the remediated portion of the aquifer was such that a less extensive zone of low D.O. concentrations was produced. It is unclear which of these mechanisms has caused the size reduction of the anoxic zone.

In summary, aquifer heterogeneities and biodegradation caused the centre of mass to behave unconventionally after sufficient time had passed such that the slug size was quite small and chromatographic separation of the different componds had occurred. There is a strong correlation between centre of mass movement and the availability of oxygen at the slug rear. It should be noted that these anamolous velocity effects are for a contaminant slug and are not necessarily indicative of the behaviour of a plume emanating from a gasoline source.

3.14 MASS ESTIMATES

Mass of BTEX, chloride and nitrate remaining in solution was estimated using the method of moments (Freyburg, 1986). Data are presented in the form of plots of mass remaining in solution with time. Regression analyses using Statistical Analysis System (SAS), a statistical software package, were performed to obtain time rates of mass change.

3.14.1 Chloride and Nitrate

Chloride and nitrate masses remained constant with time until day 113 (Figure 3.21(b)) and perhaps beyond. During the last two snapshots (days 113 and 148), the chloride/nitrate slug was not completely sampled at the outer edges and this apparently resulted in only about 80% to 90% of the original mass being accounted for. The mass loss may also partly be due to dilution below detection.

The relatively constant nitrate mass observed until day 113 is inconsistent with the results of laboratory Experiments 2 and 3 from which it was concluded that the organic matter in the aquifer material alone had a high nitrate demand. However, the aquifer material obtained for the experiments was from a narrow depth interval and is not necessarily representative of the entire aquifer. Because of the error in the mass estimate at late times, nitrate mass loss was not detectable.

Nitrate is a pollutant so its fate must also be established during the remediation of gasoline-contaminated groundwater. Although decreases in the nitrate mass in solution were not detected, the maximum concentration of nitrate decreased with time due to dispersion. On day 148, over 300 groundwater samples were found to contain nitrate at concentrations greater than background (about 0.07 mg/L NO_3^- as N) but only one sample contained nitrate at a concentration greater than the recommended drinking water limit of 10 mg/L N as NO_3^-. This sample contained a nitrate concentration of 16 mg/L (N as NO_3^-) and represents a threefold dilution of the original injection water. Periodically, samples were analyzed for nitrite, another pollutant, and those samples contained less than 1 mg/L nitrogen as nitrite.

3.14.2 BTEX

After 148 days, over 95% of the injected BTEX mass was removed from both unremediated and remediated slugs. Dilution of BTEX to below detection (approximately 1 ug/L) could have resulted in the loss of up to 20% of the mass if dispersion of BTEX was similar to that of chloride. However, concentration gradients within the BTEX slug were much sharper than those within the chloride slug because of biodegradation at the outer fringes of the slug. Sampling and analyses were performed to investigate the presence of BTEX at concentrations less than 1 ug/L. The results, presented in section 3.17, confirm the suggestion of complete removal during biodegradation. It can be concluded that dispersion of BTEX to concentrations below detection was an insignificant process causing mass loss since biodegradation reduced the concentrations of BTEX at the slug fringe to well below 1 ug/L.

Table 3.10 lists the masses of the aromatic compounds remaining in solution on day 148. The error in calculation of mass increases with decreasing mass because the piezometer density to plume size ratio increases (Bumbalis et al., 1987). Masses which are reported as less than 10 ug may suffer from up to 200% error while masses greater than 10 ug may suffer from as little as 25% error.

Total BTEX mass remaining in solution after 148 days was essentially the same for both unremediated and remediated cases. The differences in remediated and unremediated individual masses are generally slight, however, remediated toluene and m-xylene masses are less than the unremediated and the unremediated benzene mass is much less than the remediated mass. The large remediated benzene mass remaining may have been the result of the recalcitrance of benzene during biodegradation but it did not appear to be more recalcitrant during laboratory experiments.

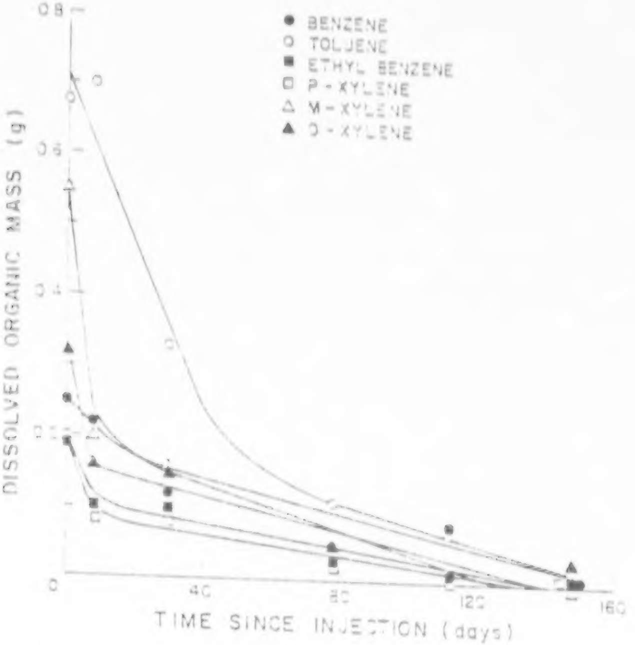
Table 3.10: Mass Remaining in Solution on Day 148 (mg)

	Unremediated	Remediated
Benzene	7.8±2.1	49.5±5.5
Toluene	14.8±3.4	0.5±0.3
Ethyl Benzene	5.5±2.7	0.5±0.3
P-xylene	10.4±2.4	5.7±2.7
M-xylene	2.7±1.3	0.1±0.1
O-xylene	21.8±5.0	19.3±4.4
Total BTEX	63±17	76±13

Figure 3.21 (a) and (b) are plots of the dissolved organic solute masses remaining in solution as a function of time. The initial data points were obtained by sampling the input solution prior to injection and therefore represent total mass injected. All other data points were obtained from sampling the groundwater and are representative of only the organic mass in solution. The mass loss curves illustrated do not distinguish organic mass losses due to biodegradation from losses due to sorption. The organic mass sorbed to the solid phase was calculated using distribution coefficients determined from the retardation factors of unremediated BTEX (Table 3.8) and the mass of organics in solution on day 8 (Figure 3.18). Sorptive losses during the first 8 days were calculated to be about 20% of the total BTEX mass injected approximately the same as the observed mass losses. M-xylene may be the one exception with observed losses at least twice that of the predicted sorptive losses. Perhaps biodegradation of m-xylene began sooner than it did for the other compounds.

Figure 3.21: Estimates of the total dissolved mass of the solutes remaining in the groundwater up to 148 days after injection (a) unremediated BTEX (b) remediated BTEX, chloride and nitrate

(a)



(b)

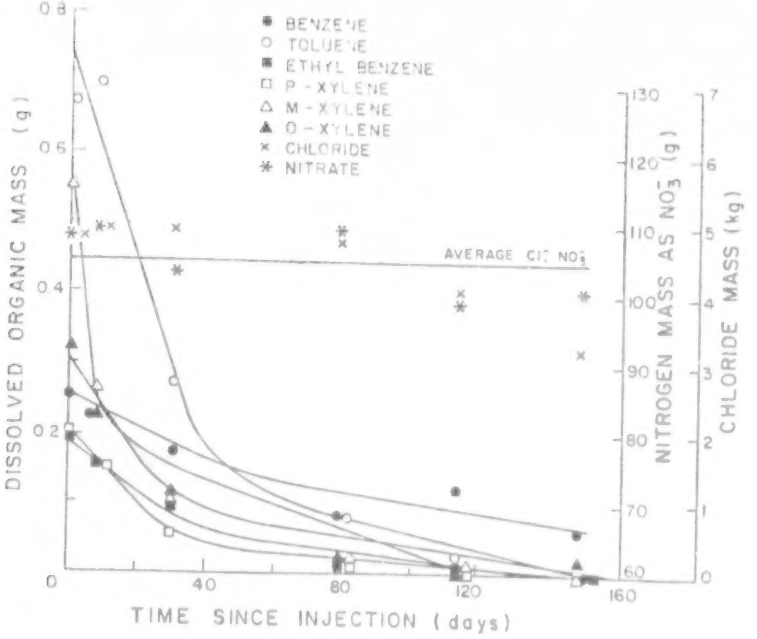


Table 3.11: Sorptive Losses for BTEX for days 0 - 8

Compound	Kd	Equilibrium Conc. (g/m^3)		Mass Sorbed $(g/g \times 10^6)$		Total Sorbed/ Mass Lost	
		Unr	Rem	Unr	Rem	Unr	Rem
Benzene	.000	.09	.10	0	0	0	0
Toluene	.023	.28	.28	.006	.006	*	*
Ethyl Benzene	.068	.04	.04	.003	.004	0.50	1.25
P-xylene	.113	.04	.06	.004	.007	0.45	1.60
M-xylene	.113	.08	.10	.009	.012	0.31	0.48
O-xylene	.113	.06	.09	.007	.009	0.56	1.10

Kd= distribution coefficient (Patrick et al., 1985)
Equillibrium concentration = day 8 mass/2500 L
* - No losses observed

The sorptive losses were calculated for the period of 8 to 30 days to determine sorptive loss due to increased slug volume as a result of dispersion. The organic mass removed from solution due to sorption was insignificant when compared to the observed mass loss. It can be assumed that mass losses after day 8 were primarily due to biodegradation. These findings were consistent with laboratory results indicating a short lag period preceeded BTEX removal by aerobic biodegradation.

Each mass loss curve consists of a steep initial segment where the mass loss rate was constant through time, followed by a rate reduction or tailed section. Tailing of the mass loss curves is consistent with observations of BTX mass loss summarized by Patrick et al. (1986). Both zero and first order biodegradation rates are commonly reported in connection with the transformation of aromatic hydrocarbons in laboratory experiments (Ward and Thomas, 1986). Zero order rates imply no dependancy of the rate upon the initial mass or concentration present and resulting mass loss curves are linear. First order rates imply a dependancy of the reaction rate upon the initial mass or concentration and resulting mass loss curves are exponential. Thus the mass loss curves could be interpreted as reflecting a change from zero to first order biodegradation kinetics.

Tailing is also consistent with biotransformation processes, on a laboratory scale, in which the mass loss approaches a threshold concentration (Alexander, 1985). Mass loss does not continue past this minimum concentration or may continue at a very reduced rate due to cometabolism (McCarty et al., 1981). The threshold concentration theory is addressed in a subsequent section however, this does not appear to be the reason for the tailing of the mass loss curves. Tailing of the mass loss curves obtained from the field experiment may not be the result of the specific biodegradation processes. Instead, the tailing may simply be due to the dynamic aspects of the experiment. Barker and Patrick (1985) suggest that oxygen availability, and not the overall homogeneous biodegradation rate obtained from laboratory experiments, controlled the rate of BTX mass losses in the previous field injection experiment. They warn that attributing a reaction order to the biotransformation process based on field scale mass loss curves is not a straightforward process. Borden et al. (1986) suggested that oxygenation of a hydrocarbon plume, not biodegradation rates, limited the mass lost at a creosoting site. This suggestion is consistent with the modelling results presented in Chapter IV of this report which conclude that oxygen limitation controls the rate of mass loss.

In order to describe the observed mass losses mathematically, two different regression analyses were performed. The first analysis used linear regression while a later analysis used first order regression. A steep line was fitted to the first 3 or 4 data points for each solute and a line with reduced slope was fitted to the remaining points. This zero order model, in which each mass loss curve was fitted using two lines, is illustrated in Figure 3.21. However, zero order mass loss rate constants and R-square values obtained from linear regression are presented in Table 3.12. R-square is a measure of how much variation in mass is accounted for by the regression model. In general, the larger the R-square value, the better the model's fit (SAS Institute, 1982). R-square values are 0.79 or greater indicating a good fit of the model. Zero order mass loss rates are difficult to obtain because of a subjectivity introduced when splitting the curve into two linear segments.

Alternatively, the mass loss data may be described using first order mass loss rates in which a logarithmic curve is fitted to the data. First order rate constants and R-square values from regression analyses are presented in Table 3.12. Although R-square values obtained for the first order rate model are not much different from the zero order models, this model is preferred to the zero order model because of the non-subjectivity.

All remediated compounds, except benzene, disappeared at rates (first order) greater than the comparative unremediated compounds. However, the only significant enhancement of the remediated rates are shown by toluene and m-xylene, which show remediated rates to be nearly double the unremediated rates..

In section 3.13.1, it was suggested that the presence of nitrate overlapping the rear of the remediated BTEX slug enhanced mass removal at the slug rear which caused the centres of mass to be displaced forward. However, the mass estimates indicate only toluene and m-xylene removal was significantly enhanced. These organics were not located at the rear of the slug where the enhaced mass removal might be expected. Thus, this discrepancy is likely due to the large error in mass estimation compared to the relatively smaller error in the estimation of the centre of mass.

Table 3.12: Mass Loss Rates for Unremediated and Remediated BTEX

	Zero Order			First Order	
	Rate-1 (-mg/d)	Rate-2 (-mg/d)	R^2	Rate ($-d^{-1}$)	R^2
Benzene					
Unremediated	2.58	0.12	.86	.019	.84
Remediated	2.28	0.77	.81	.010	.86
Toluene					
Unremediated	12.50	1.28	.94	.024	.98
Remediated	14.65	1.14	.91	.043	.92
Ethyl Benzene					
Unremediated	10.00	0.81	.93	.024	.93
Remediated	3.56	0.64	.86	.037	.96
P-xylene					
Unremediated	13.75	0.67	.90	.023	.78
Remediated	4.90	0.35	.79	.027	.82
M-xylene					
Unremediated	43.75	1.53	.92	.034	.97
Remediated	36.25	1.65	.81	.060	.92
O-xylene					
Unremediated	2.00	0.12	.94	.019	.87
Remediated	6.57	0.76	.79	.021	.83

3.15 COMPARISON OF BTX AND BTEX BEHAVIOUR

The influence of non-BTEX dissolved gasoline components on biodegradation processes occurring in the field were obtained through comparison of the results of this study to results of the previous injection experiment described by Patrick (1985). Although both studies involved the injection of water containing monoaromatic hydrocarbons, the injection waters differed in initial concentrations, source of the monoaromatics, volume, and dissolved oxygen content. These differences are listed in Table 3.13.

The mass loss curves obtained for BTX (Patrick, 1986) and unremediated BTEX of this study both show steep initial declines followed by tailing or apparent first order mass loss. Table 3.14 lists the first order mass loss rates determined for Patrick's BTX mass loss data and unremediated BTEX. Generally, differences between the rates are slight although gasoline-derived toluene was removed at a slower rate than pure, dissolved toluene. Pure dissolved BTX and BTEX dissolved from gasoline were similarly removed from solution in the field.

Table 3.13: Comparison of BTX^1 and BTEX^2 Injection Solutions

PARAMETER	BTX^1	BTEX^2
total BTX conc (mg/L)	7.5	0.7
Volume injected (L)	1800	2500
Average D.O. conc. (mg/L)	1.3[illegible]	2.30
Average water temp. (^{0}C)	23.7	15
Source of monoaromatics	pure compounds	gasoline
Date of injection	August, 1984	June, 1986

1 - Patrick et al. (1985,1986)
2 - This study

Results from microcosm experiments discussed by Berry-Spark et al. (1987) and from Experiment 4 suggest that BTX mass loss should have occurred at a much greater rate than BTEX mass loss, yet, such differences do not exist in the field results. The discrepancy between laboratory and field results may be due to the physical behaviour of the BTEX slug in the field. With time, the gasoline components could separate along the direction of flow because of differing retardations. Although there would still be some competition for oxygen amongst the organics, the impact of other gasoline-derived organics on BTEX degradation would be lessened by their physical removal.

The similarity in BTX and BTEX mass loss rates observed in the field results may be a coincidence which occurred because of the very low initial BTEX mass. Although differences in BTX and BTEX mass removal rates were minimal, the advective behaviour of BTEX differed greatly from that of BTX. BTEX centres of mass apparently stopped advecting after 78 days while BTX centres of mass advected at velocities which were consistent with sorptive retardation. Other more retarded gasoline constituents were thought to have biodegradaed and limited the oxygen available at the rear of BTEX for biodegradation. The effect on BTEX mass removal was minimal because it occurred after most of the BTEX had already been removed. Had substantial BTEX mass remained in solution after 78 days, a considerable slowing of mass removal rates may have occurred. Although not shown in this comparison, the presence of other gasoline derived organic compounds are likely to cause a slowing of the biodegradation of BTEX and may have a profound effect on the distribution and relative mobility of BTEX in groundwater.

Table 3.14: Aerobic Biodegradation Rates For BTX[1] and BTEX[2]

	First Order Rate Constants (d^{-1})	
	BTX[1]	BTEX[2]
Benzene	-.011	-.019
Toluene	-.044	-.024
P-xylene	-.033	-.023
M-xylene	-.033	-.034
O-xylene	-.027	-.019

1 - determined from data of Patrick et al. (1986)
2 - this study

3.16 BTEX BIODEGRADATION IN THE LABORATORY AND FIELD

Biodegradation of BTEX in the laboratory and field is comparative in terms of processes and relative rates. Biodegradation rates cannot be directly compared because biodegradation rates were determined in the laboratory but mass loss rates were obtained from the field. Mass loss rates may not be indicative of small scale biodegradation processes because of control of the mass loss rates by solute mixing within the aquifer.

Denitrification was not confirmed in the field because the acetylene block technique was not used. Its occurrence may be inferred through the additional BTEX mass lost from the remediated slug but this may also have been due to nitrate enhancement of the aerobic mass loss rates. The mobility of remediated BTEX in the field seemed to have been controlled by the distribution of dissolved oxygen even when nitrate overlapped the rear of the organic slug. When nitrate and oxygen were present at the rear of the remediated slug, mass removal occurred preferentially at the BTEX slug rear. When only nitrate was present at the slug rear, mass loss occurred preferentially from the BTEX slug front. These findings suggest that if BTEX removal occurred strictly during denitrification, the rate of removal was slower than the aerobic rate of removal. Removal rates when both oxygen and nitrate were present were faster than aerobic rates. These interpretations are consistent with the results of the laboratory studies.

3.17 INVESTIGATION OF THE BTEX THRESHOLD THEORY

Biodegradation resulted in the removal of over 95% of the BTEX mass in both remediated and unremediated scenarios within 148 days. The removal of the remaining dissolved BTEX may have been limited depending upon the microbial utilization processes.

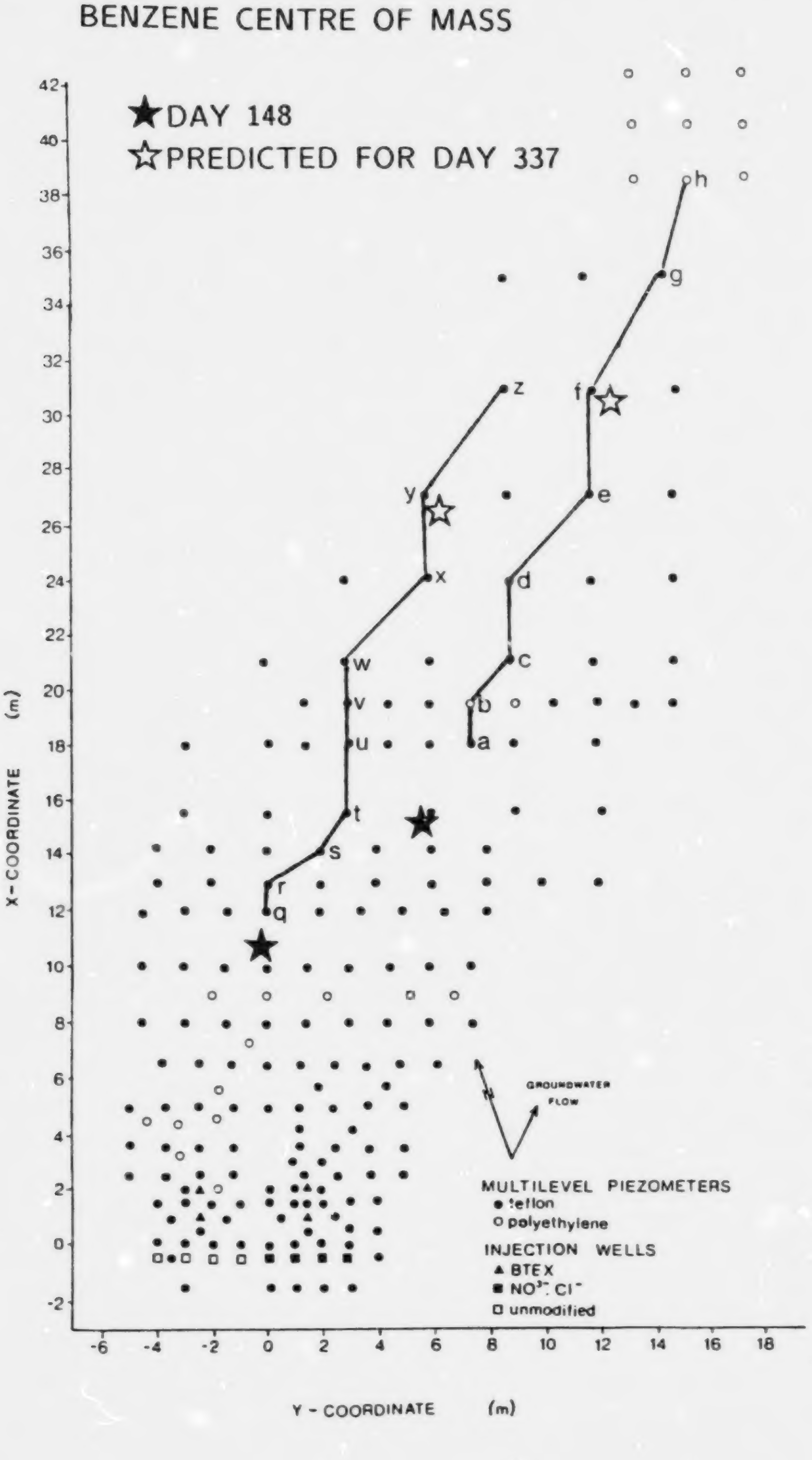
A sampling program was designed to investigate the threshold theory described in Chapter II. If biodegradation reduced BTEX to threshold concentrations (about 1 ug/L for each monoaromatic), then a residual BTEX slug would gradually replace the original BTEX slug (>1 ug/L for each monoaromatic) with time. This residual slug would become dispersed and would consist of sub-threshold concentrations of BTEX. Alternatively, as discussed in Chaper II, BTEX could persist in anaerobic zones because of slow biodegradation rates. The zones of low oxygen concentrations within the aquifer were monitored along transects parallel to flow, to encounter the widespread sub-threshold plume, if present.

Both gasoline-contaminated slugs were sampled approximately one year after injection to determine if biodegradation had produced persistent low, but detectable, levels of BTEX. Samples were concentrated using a purge and trap technique and analyzed using gas chromatography and mass spectrometry (PT-GCMS) with detection limits in the 0.040 to 0.001 ug/L (40-100 ng/L or "ppt") range. Details of the sample preparation and analytical procedure are given in Appendix B.

D.O. distributions were determined on May 13, 1987 by sampling along two transects parallel to flow (Figure 3.23). BTEX was previously shown to persist in zones of low D.O. concentrations so such zones were targets for BTEX sampling (Figure 3.24). On May 20 and June 17, 1987 (337 and 365 days after the BTEX injection), a total of 34 samples were retrieved for PT-GCMS BTEX analysis. 60 cm^3 samples were retrieved using the modified vacuum manifold (described in Chapter II) from target piezometers along the transects. Sample water contacted only glass, stainless steel, and teflon during sampling. Prior to the retrieval of each sample, the hardware contacting the sample water was carefully cleaned by pumping 50 cm^3 of methanol and 1 L of deionized water through the sampling equipment, to eliminate cross-contamination of samples. Organic-free deionized water was similarily sampled in the field to confirm that cross-contamination of samples did not occur. This water was analyzed both before and after contacting the sampling equipment. The samples were preserved with 0.6 cm^3 of a 10% sodium azide solution and were capped using teflon-faced silica septa. The tedious sampling procedure and costly analyses did not allow comprehensive snapshot data to be obtained in this way. Data were corrected for laboratory blanks as described in Chapter II.

The distribution of compounds was spotty but there was a general correlation between zones of low D.O. concentration and BTEX persistance (Figure 3.24) Benzene was the most persistent of the organics and was found in excess of 1 ug/L in samples from both transects. Toluene was found in only one sample taken from the unremediated portion of the experiment, at a concentration of 1.4 ug/L. P-xylene was present in two samples from this transect but concentrations were below 1 ug/L. All other samples contained no detectable BTEX.

Figure 3.22: Cross-section locations and predicted benzene centres of mass



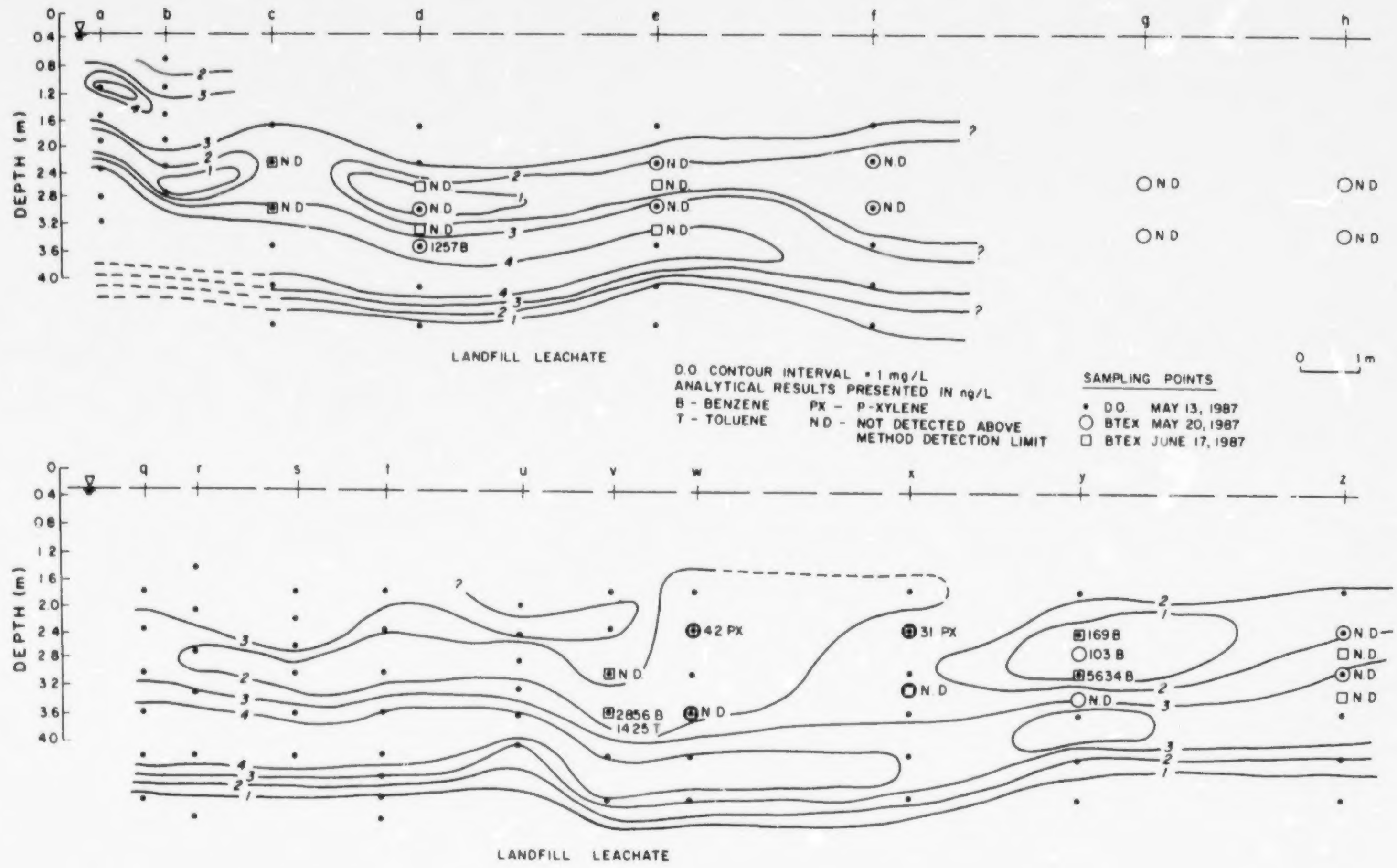


Figure 3.23: Vertical sections illustrating oxygen distributions and low level BTEX concentrations. (a) remediated (b) unremediated

The isolated occurrences of BTEX along the transects suggests that the biodegradation processes which occurred within the aquifer did not result in the production of threshold levels of BTEX. A large plume of sub-threshold level BTEX was not identified. The presence of benzene, toluene, and p-xylene in some of the samples may be attributed, instead, to the recalcitrance of these compounds where their removal was limited by the low D.O. concentrations.

3.18 SUMMARY OF FIELD EXPERIMENT RESULTS

The results of the field and laboratory studies described herein provide insight into the fate, persistence and mobility of gasoline-derived BTEX in shallow, aerobic sand aquifers in both the presence or absence of nitrate.

The results of the unremediated field experiment were used to determine the natural behaviour of gasoline-derived BTEX in groundwater. Retardation factors for BTEX prior to day 78 were calculated from the centre of mass movement and were similar to those obtained from small scale laboratory tests (Patrick et al., 1985) and a previous field test using pure dissolved BTX (Patrick et al., 1986) indicating that the non-BTEX dissolved components of gasoline did not influence retardation of BTEX at the concentrations used in this field experiment, initially.

After 78 days, advection of the BTEX centres of mass apparently ceased. It was concluded that this was the result of the small BTEX slug size combined with aquifer heterogeneities and oxygen limitation. Such phenomena did not occur previously with BTX. It was suggested that the presence of more retarded gasoline-derived organics lagging behind the BTEX slug limited the oxygen available at the slug rear so mass removal occurred predominantly at the slug front. The non-uniform mass removal caused a stagnation in the centre of mass movement even though the solutes actually continued to move via advection.

Biodegradation of BTEX in laboratory microcosm experiments was significantly slowed by the presence of other gasoline-derived organics but field scale mass loss rates for BTEX appeared about the same as those observed for pure dissolved BTX (Patrick et al., 1986). Perhaps the physical separation of the dissolved gasoline compounds due to differing retardations allowed the removal of the compound(s) which limited BTEX degradation rates in the microcosms, thereby leaving BTEX unaffected by their presence in the field.

The injection water contained less than one half the desired BTEX concentration and the resulting BTEX mass decreased rapidly prior to the complete overlap of the nitrate and BTEX slugs. Nitrate mixed with the BTEX within the aquifer under natural hydraulic conditions primarily because of dispersion however, differences in solute advective velocities allowed the nitrate slug to overtake the BTEX slug. Both nitrate and BTEX tended to occupy similar layers. Dissolved oxygen was limiting in these layers because of its involvement in biodegradation. The conditions for denitrification (low D.O. concentrations, available organic carbon and nitrate) appeared to have been met by day 78 so denitrification may have occurred.

After 148 days, the BTEX mass remaining in solution was the same for both unremediated and remediated experiments. Toluene and m-xylene removal from the remediated slug was enhanced while benzene removal was impeded in comparison to removal from the unremediated slug. The error involved in calculating masses was large at late times becuase of the small slug size and thus the effect of nitrate addition was not significant enough to produce detectable enhancement of BTEX removal in this case.

The use of nitrate as an electron acceptor during BTEX biodegradation in an oxygen deficient environment was not successfully evaluated during the field experiment. However, it was demonstrated that nitrate could be injected into and mixed with BTEX contaminated groundwater using the natural transport processes of advection, dispersion and sorptive retardation. If the microbiological process can be more successfully stimulated, this nitrate addition procedure has great remedial potential.

Chapter IV

BTEX BEHAVIOUR IN OTHER HYDROGEOLOGIC SETTINGS

In this chapter, the results of the Phases II and III research studies are applied to the prediction of the mobility and persistence of BTEX in other hydrogeologic settings. Numerical models, which were previously developed and are described by MacQuarrie et al. (in submission), were employed. The required information was generated by considering BTEX behaviour for ranges of values of important hydrogeologic and biogeochemical parameters such as groundwater velocity, initial oxygen content, retardation, and bacteria population. A model sensitivity analysis, sponsored by PACE, was performed to determine the parameters having the greatest influence on the fate, persistence and mobility of BTEX in groundwater.

A two-dimensional finite element model (MacQuarrie et al., in submission) was used to simulate the transport of an organic solute (toluene) and oxygen. Three advection-dispersion equations (Freeze and Cherry, 1979) were solved simultaneously to describe the transport and interaction of oxygen, an organic solute and indigenous bacteria. The equations incorporated linear retardation, dual-Monod biodegradation kinetics and bacterial growth where applicable. The major assumptions used during this modelling study are:

1. All solutes are dilute and are transported in a saturated, incompressible porous media.
2. Retardation of organics is linear with local equillibrium.
3. Dissolved oxygen is the sole electron acceptor.
4. Sorbed organic mass is not available for biodegradation.
5. The majority (>95%) of the microbial population is adapted and immobile.
6. Microbial dynamics are unaffected by pH, temperature or secondary substrate utilization.

A complete discussion of the theory, formulation and boundary conditions is given by MacQuarrie et al. (in submission).

The situation addressed in this modelling study is for a short injection of hydrocarbon-contaminated groundwater with the movement and fate of the hydro-

Table 4.1: Parameters for Homogeneous Aquifer Sensitivity Analyses

	BASE VALUE	RANGE
PHYSICAL PARAMETERS		
Hydraulic Conductivity (m/sec)	10^{-4}	10^{-3}, 10^{-5}
Hydraulic Gradient	0.005	--
Porosity	0.35	--
Velocity (m/day): horizontal	0.09	0.9, 0.009
vertical	0.00	--
Dispersivity (m): longitudinal	0.81	--
transverse	0.005	0.000,0.05
Background D.O. conc. (mg/L)	3.5	1.0,6.0
Initial Toluene conc. (mg/L)	3.0	0.3 30.0
Oxygen diffusion coefficent (m^2/day)	$5.2\text{x}10^{-5}$	--
CHEMICAL PARAMETERS		
Fraction of organic carbon (%)	0.028	0.000,0.1
Retardation factor	1.4	0.0,2.1
BIOLOGICAL PARAMETERS		
O_2:Toluene utilization ratio	3:1[	--
Monod kinetic parameters		
k (d^{-1})	0.493	4.928,0.049
K_s(ug/L)	654	65.5,6545.8
O_2 half utilization constant (mg/L)	0.1	--
Microbial yield	0.426	--
Decay coefficient	0	--
Initial bacteria conc. (mg/1000 cm^3)	0.23	2.3,0.023

carbon determined over time. This is analogous to the injection experiments conducted in the Borden sand aquifer and does not represent any particular actual groundwater contamination scenario. In the modelling study, however, parameter values typical of other settings are employed.

To study the sensitivity of biodegradable organic transport to various physical, chemical and biological parameters, a base case was selected to represent the conditions of the Borden field experiment with uniform horizontal groundwater flow. Simulations were performed for homogeneous vertical sections of the aquifer by varying a single parameter and maintaining all other input parameters at their base case values (Table 4.1). The physical parameters reflect those obtained by Sudicky (1986) for the Borden aquifer, chemical parameters were obtained from Patrick et al. (1985), while biologic parameters were obtained by callibrating the model with a laboratory column experiment (MacQuarrie et al., in submission) similar to that described in Chapter III. A spatial moment analysis was applied to the organic distributions to determine the mass in solution and centre of mass movement.

The effect of heterogeneities was investigated by generating random hydraulic conductivity fields based on statistical properties of the Borden aquifer and using pore-scale dispersivities for transport. Model results using the Borden aquifer statistical parameters (Sudicky, 1986) are compared to other hypothetical aquifers with different structures.

The reader will have to define or predict the values of the important parameters at the site of interest and then review the information presented in this chapter in order to estimate the likely behaviour of BTEX. This approach should help the reader properly conceptualize the hydrogeological setting and contamination problem and should also assist in the design and implementation of subsequent site investigations.

4.1 SENSITIVITY ANALYSIS OF ORGANIC PLUME BEHAVIOUR IN UNIFORM FLOW FIELDS

4.1.1 Initial Organic Concentration

Figure 4.1 shows the normalized mass in the organic plume as a function of time for three different initial organic concentrations. Because the initial mass in each organic slug is different, the mass is normalized by dividing the dissolved mass in the organic plume by the dissolved mass at time zero. The injection concentration of 30 mg/L is approximately an order of magnitude less than the solubility of toluene in water (Kebe et al., 1974). The plume originating from the 30 mg/L initial injection experienced mass loss, but at a slower normalized rate than that of the other two cases in which the initial concentration is less. Although the 30 mg/L plume may persist until 1000 days, the 0.3 mg/L plume completely degraded prior to 100 days of travel time. Because the kinetic biodegradation parameters were identical for all three cases, mass loss was not controlled by biodegradation alone.

Figure 4.2 and Figure 4.3 show the organic plumes and the dissolved oxygen distributions, respectively, for the 3 mg/L and 30 mg/L injections. The plume injected at 30 mg/L occupies a large area of the aquifer and maintains relatively high concentrations until 200 days. The corresponding region of oxygen depletion, below the background of 3.5 mg/L, is much larger than that for the lower concentration injection case. Because oxygen is being consumed for biodegradation at a relatively rapid rate along the fringes of the initially high organic concentration plume, the depletion of oxygen is limiting the organic solute mass loss. For the initially low organic injection case on the other hand, oxygen does not become limiting to the same extent and biodegradation proceeds in an unimpeded manner. Oxygen transport from the water table does not contribute significantly to the

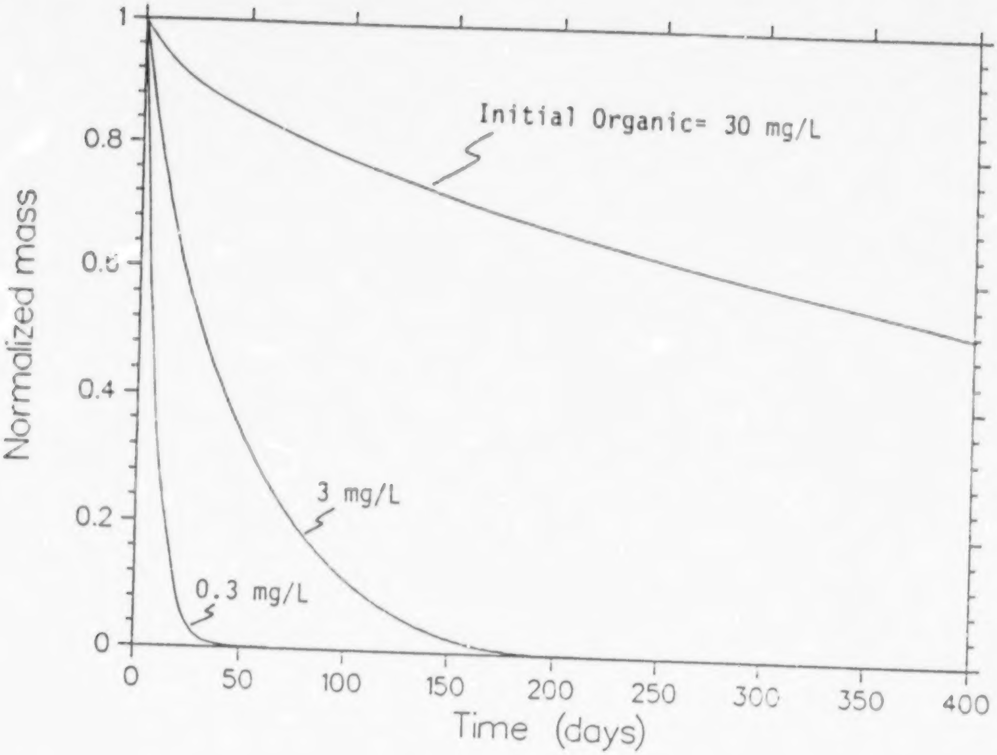


Figure 4.1: Normalized Organic Plume Mass versus Time for Three Initial Organic Injection Concentrations.

biodegradation of either plume due to the limited downward diffusion of dissolved oxygen from the water table.

As shown in Figure 4.2, the position of the center of mass of the base case organic plume is further downgradient than that of the higher initial concentration plume. The horizontal velocity of the 3 mg/L plume is 0.086 m/day while that of the 30 mg/L plume is about 0.073 m/day. The mass loss rate at the upgradient end of both organic plumes will be greater than at the leading edge of the plume because the microbial population will be slightly larger at the trailing edge of the organic plume. This causes the center of mass to be shifted down gradient. The higher initial concentration plume, however, consumes oxygen very rapidly at its upgradient end. This limits mass loss and causes the shifting of the position of the center of mass to be less than for the lower concentration plume.

The small size of the 3 mg/L plume at 200 days is due to biodegradation which limits the spreading caused by dispersion. The 30 mg/L plume on the other hand, exhibits little reduction in its vertical thickness while the longitudinal extent of the plume after 200 days is large compared to the lower initial concentration

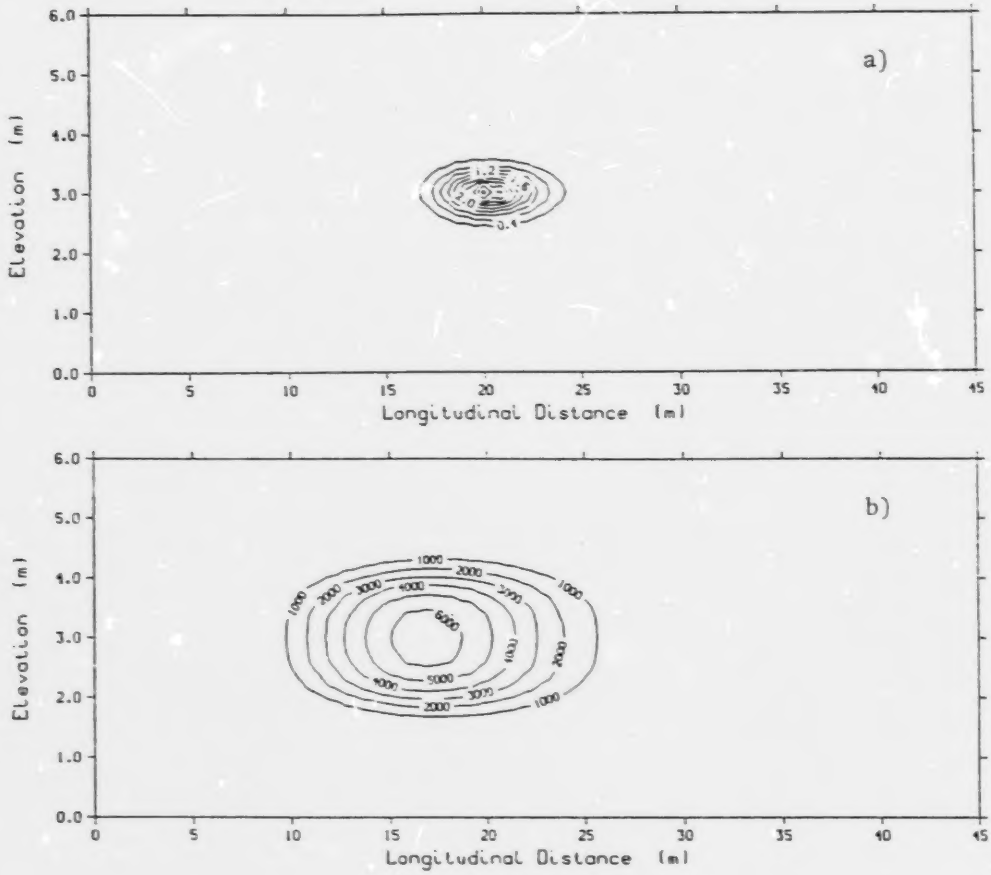


Figure 4.2: Model Prediction of Organic Plumes at 200 days; a) Initial Organic Conc. of 3 mg/L, b) Initial Organic Conc. of 30 mg/L. Concentration Isolines are in ug/L.

plume. The rapid consumption of oxygen limits the biodegradation at the fringes of the high organic plume such that the dispersive spreading is stronger than the shrinking due to biodegradation.

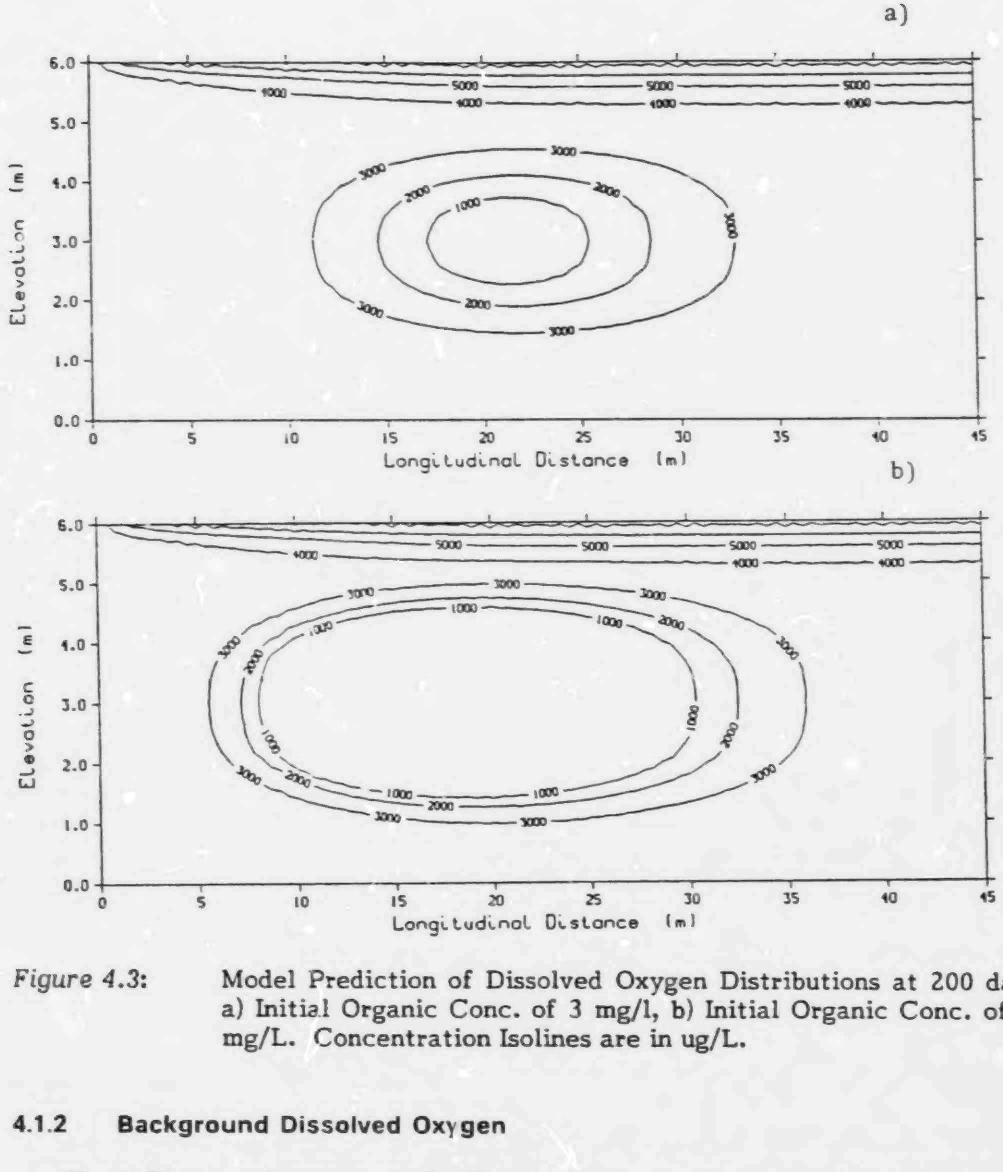


Figure 4.3: Model Prediction of Dissolved Oxygen Distributions at 200 days; a) Initial Organic Conc. of 3 mg/l, b) Initial Organic Conc. of 30 mg/L. Concentration Isolines are in ug/L.

4.1.2 Background Dissolved Oxygen

The influence of oxygen availability is illustrated by varying the initial background concentration of dissolved oxygen in the groundwater. Figure 4.4 shows the mass loss of the organic solute plume, originating from a 3 mg/L organic injection, for three values of background dissolved oxygen concentration. The results in Figure 4.4 have not been normalized because the initial organic mass is the same for each case. The range of values of dissolved oxygen for these three cases is typical of groundwaters in shallow, unconfined aquifers. Deeper geologic formations or previously contaminated aquifers may have less than 1 mg/L of dissolved oxygen. As the initial background oxygen content is reduced, the rate of mass loss from the organic plume decreases; no mass loss would occur if the the initial oxygen concentration was zero because anaerobic biodegradation is not accounted for in this model. The mass of organic remaining after 400 days is significant under the low oxygen condition of 1 mg/L. This example clearly demonstrates the importance of oxygen availibility on organic plume aerobic biodegradation.

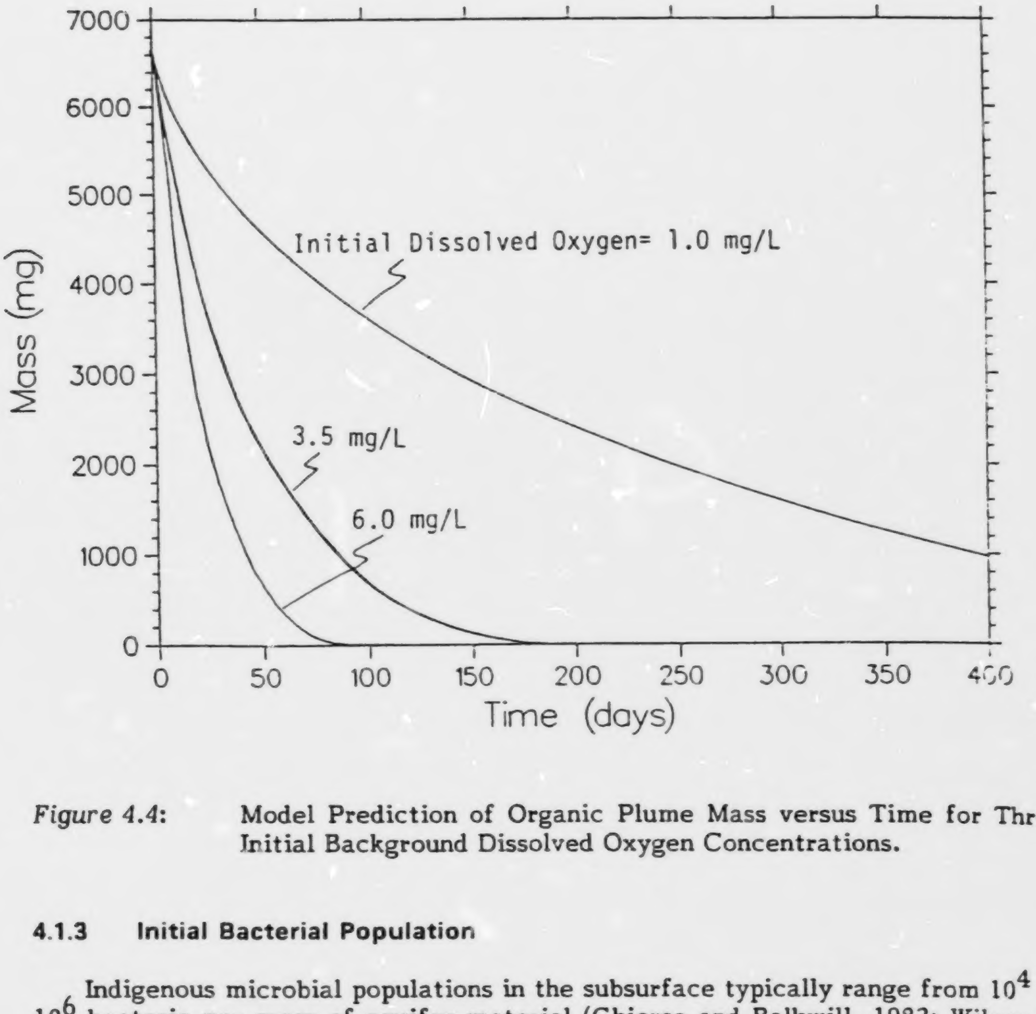


Figure 4.4: Model Prediction of Organic Plume Mass versus Time for Three Initial Background Dissolved Oxygen Concentrations.

4.1.3 Initial Bacterial Population

Indigenous microbial populations in the subsurface typically range from 10^4 to 10^6 bacteria per gram of aquifer material (Ghiorse and Balkwill, 1983; Wilson et al., 1983; Ventullo and Larson, 1985). Viable aerobic plate counts performed on cores taken from the Borden aquifer have yielded bacterial populations on the order of 10^5 per gram of sand (Berry-Spark, 1987). This corresponds to an initial background microbial concentration of approximately 0.23 mg/1000 cm^3 of aquifer material. The effect of varying the initial microbial mass is shown in Figure 4.5. As the initial population is decreased to a low value of 0.023 mg/1000 cm^3, a small lag in the mass loss occurs, followed by mass loss rates which are similiar to the base case. The lag in organic mass loss occurs during the time when the microbial population is increasing from its initially small value to a level where significant organic mass loss is effected. More tailing is also evident in the mass loss curve for the low initial microbial population. When the initial bacterial mass is increased to 2.3 mg/1000 cm^3, the organic plume is slightly more persistent when compared to the base case. The larger microbial population utilizes a proportionately larger amount of oxygen than does the population in the base case. This increased oxygen consumption results in a reduction in mass loss because oxygen is limiting biodegradation. Nevertheless, the overall effect of varying the initial biomass concentration over three orders of magnitude is relatively small. This finding is encouraging considering the practical difficulties in obtaining information on indigenous microbial populations in the subsurface.

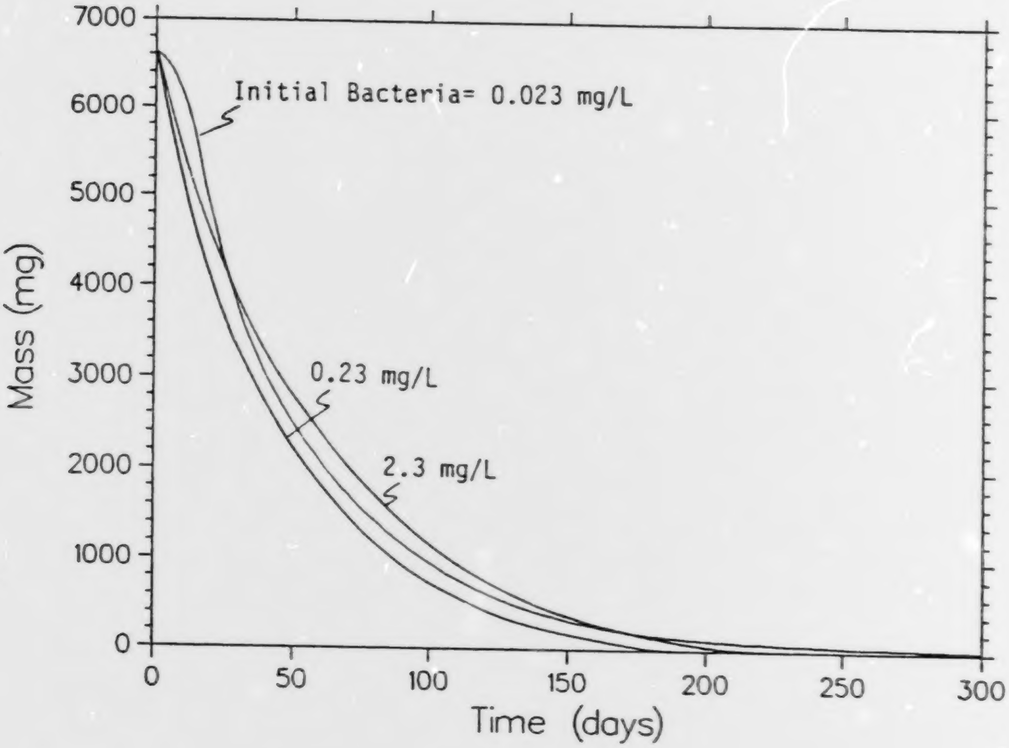


Figure 4.5: Model Prediction of Organic Plume Mass versus Time for Three Initial Background Microbial Concentrations.

4.1.4 Groundwater Velocity

By varing the hydraulic conductivity of the porous medium from 10^{-3} to 10^{-5} m/sec and maintaining a hydraulic gradient equal to 0.005 and a porosity of 0.35, the average linear velocity ranges from 0.9 m/day to 0.009 m/day. The higher hydraulic conductivity value is typical of a sand and gravel aquifer whereas the lower value might be expected in a silty sand aquifer. Figure 4.6 shows the organic mass loss over time for the three velocity cases. The rate of mass loss is much faster for the higher groundwater velocity of 0.9 m/day because of the increased mechanical mixing of the organic plume with the oxygenated groundwater.

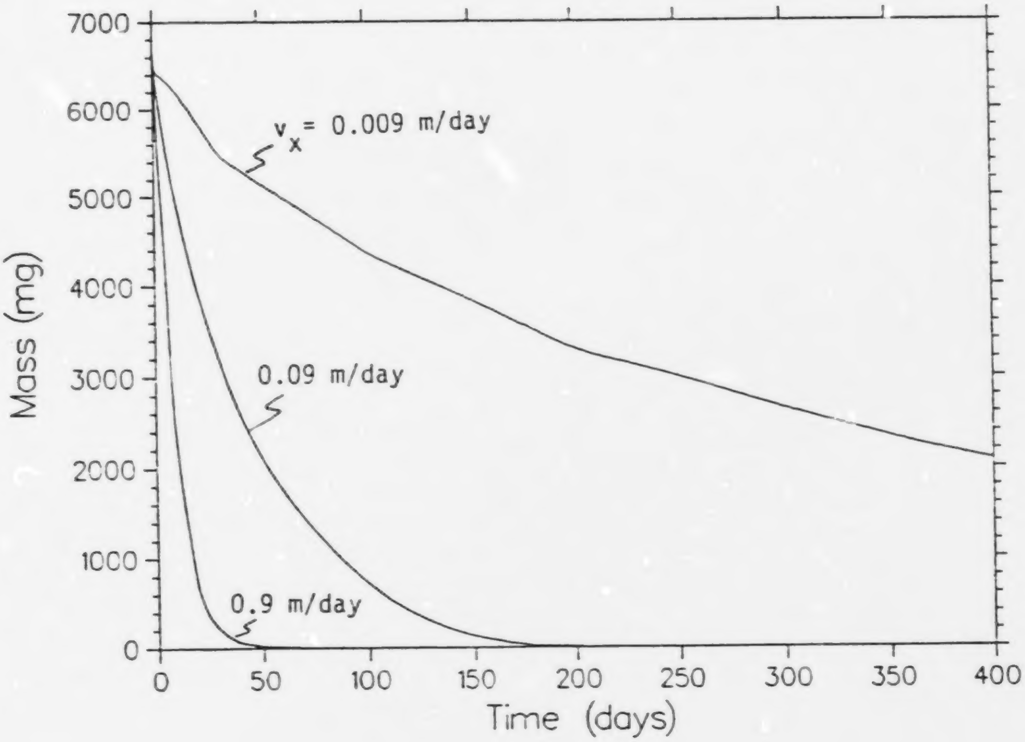
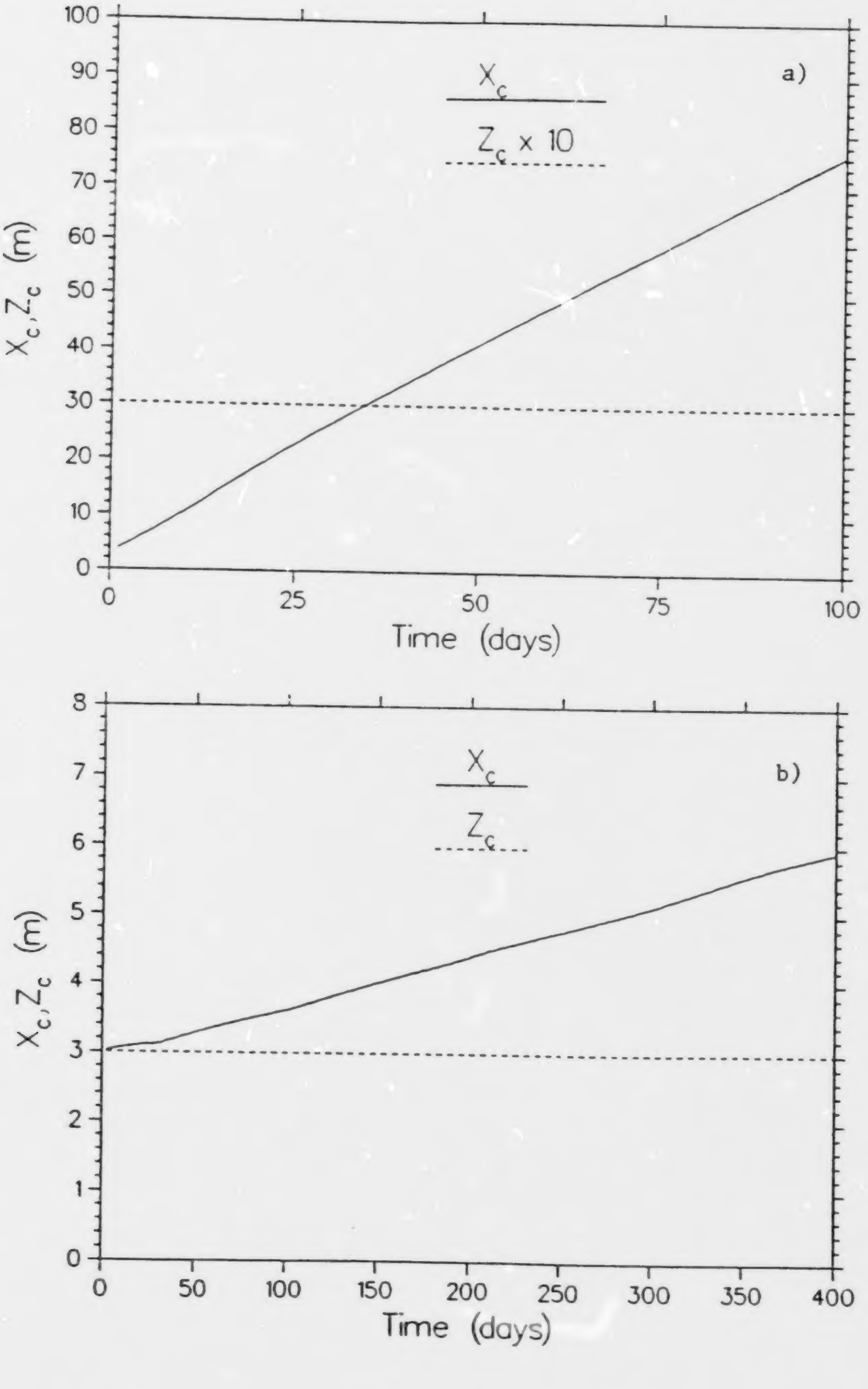


Figure 4.6: Model Prediction of Organic Plume Mass versus Time for Three Average Linear Groundwater Velocities.

Although the organic plume in the 0.9 m/day uniform flow field degrades at a relatively rapid rate, it also travels further during the time when it contains significant mass. Figure 4.7 shows the position of the center of mass versus travel time for the 0.9 m/day and 0.009 m/day simulations. Fifty days after injection the plume in the high velocity field has traveled about 41 m and has a mass of 14.4 mg. Conversely, it would take the plume in the low velocity field more than 5000 days to travel 41 m; however, extrapolating the 0.009 m/day mass loss curve in Figure 4.6 indicates that the plume will be degraded before it travels 20 m. If the position of a plume is more important than the time required for substantial mass loss, then an organic plume migrating in a high velocity field may be of more concern, even though it experiences faster mass loss.

Figure 4.7: **Model Prediction - Distance travelled by Centre of Mass of Organic Plume, (a) velocity = 0.9 m/day (b) velocity = 0.009 m/day. Xc is horizontal distance while Zc is vertical distance.**



Typical values of the vertical transverse dispersion coefficient are on the order of molecular diffusion for sandy-type aquifers in which flow is predominately horizontal (Sudicky et al., 1983). This implies that the transverse dispersivity is very small. Increasing the transverse dispersivity will increase the spreading of the organic solute in the vertical direction and will also allow more mixing with oxygenated groundwater. Figure 4.8 shows the mass loss versus time for the base case simulation (transverse dispersivity of 0.005 m) and for transverse dispersivities of 0.0 m and 0.05 m. For transverse dispersivities of less than 0.005 m, little effect on organic mass loss is observed because mechanical mixing is comparable in magnitude to molecular diffusion for such small transverse dispersivities. The value of 0.05 m, which is likely to be near an upper limit for transverse dispersivity in relatively homogeneous horizontally bedded sands, is seen to produce a slightly more rapid rate of organic mass loss. An order of magnitude increase in disperisivity only reduces the time to complete degradation by about a factor of two.

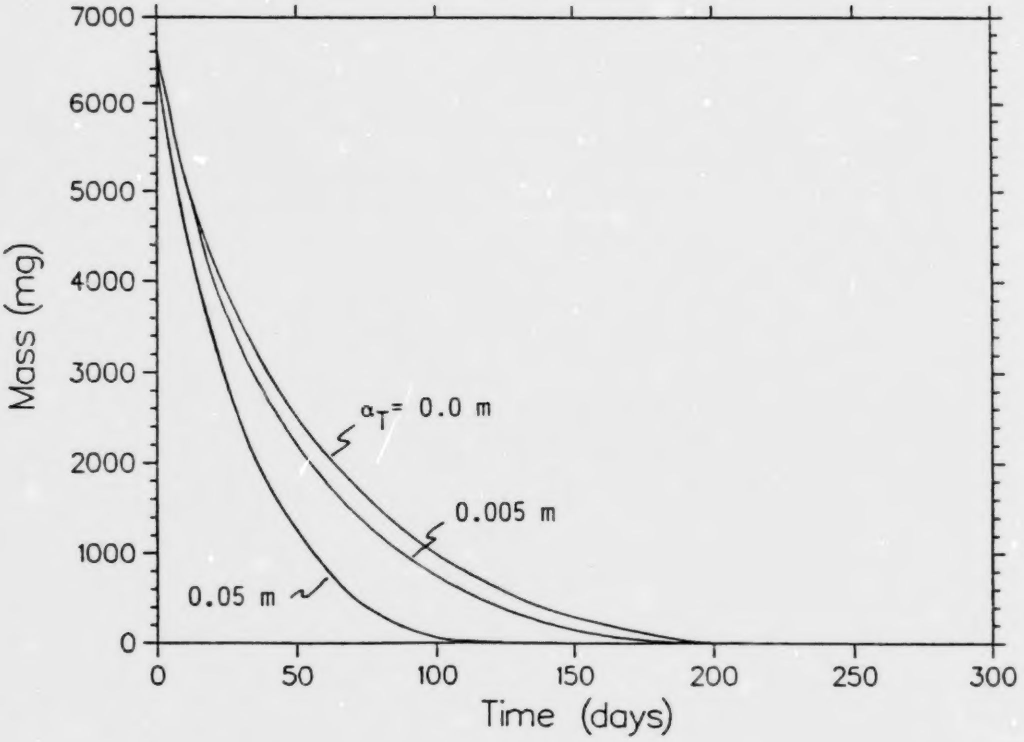


Figure 4.8: Model Prediction of Organic Plume Mass versus Time for Three Values of the Transverse Dispersivity.

4.1.5 Retardation

The Borden aquifer material has a fraction of organic carbon (foc) of 0.028% (Patrick et al., 1985). From regression equations and a variety of static and dynamic sorption tests, a retardation factor, R, of approximately 1.4 has been obtained for toluene in this aquifer material (Gillham et al., 1987). In the simulations performed here, the retardation factor ranges from 2.1 to a lower limit of 1.0, representing no sorption. The value of 2.1 is obtained for toluene by using the regression equation of Karickhoff et al. (1979) for hydrocarbon partitioning with an foc= 0.1%.

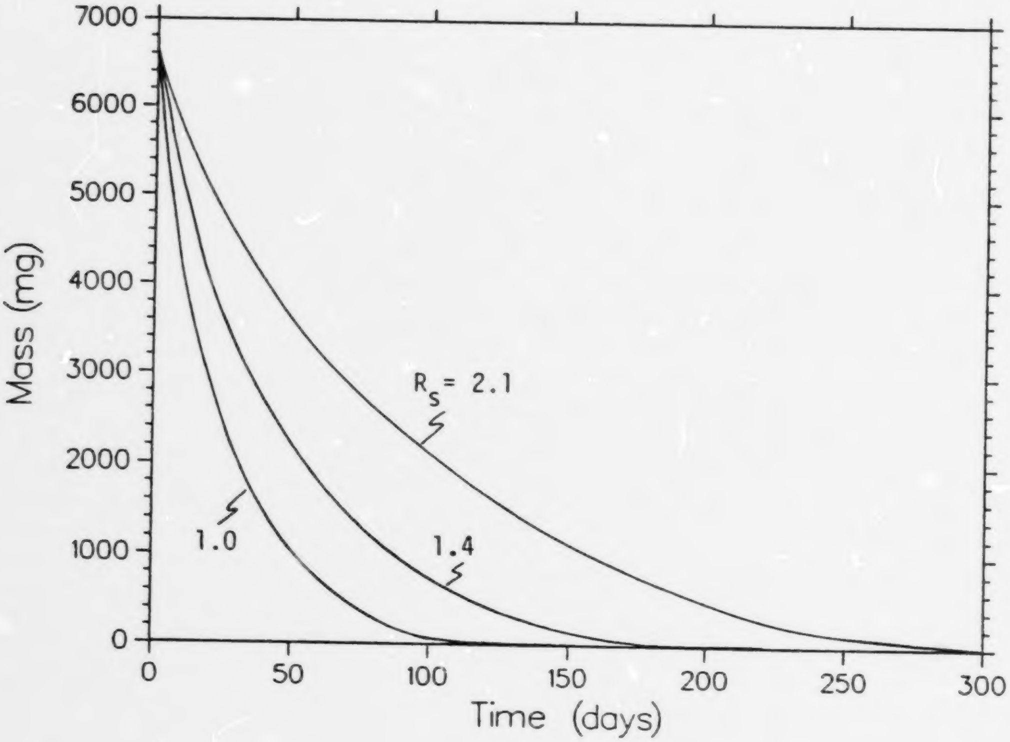


Figure 4.9: Model prediction of organic mass versus time for three organic retardation factors.

Sorbed organics were assumed to be unavailable for biodegradation. Although sorption is often regarded as an important attenuation mechanism, several studies, including those of Steen et al. (1980) and Ogram et al. (1985), have shown that a sorbed-phase organic is not available as substrate for microbial populations. Inability of bacteria to utilize organics in a sorbed state or inaccessibility of sorbed species within the soil-organic matter matrix have been suggested as possible reasons for the non-biodegradability of sorbed organic species (Ogram et al., 1985). For a retardation of 2.1, approximately 50% of the organic mass in a given volume of aquifer is sorbed and not available for biodegradation.

Figure 4.9 presents the organic mass loss for the three R values. As the retardation factor increases the rate of mass loss decreases. This trend is opposite to that which was expected based on the conceptualization of unretarded oxygen advecting past sorbed organics. If oxygenated groundwater overtaking a slower moving organic plume is a mechanism which results in increased biodegradation at the rear of an organic plume, one would expect retarded organic solute distributions to be skewed in the direction of groundwater flow. Skew (third spatial moment) was determined for the three organic plumes. The retarded plume was less skewed than the unretarded organic plume, so the expected increase in biodegradation at the rear of the retarded plume as described above was not observed (MacQuarrie et al., in submission). Apparently the increased amount of oxygen at the rear of the retarded plume is not sufficient to increase the rate of mass loss because a larger portion of organic mass is sorbed on the aquifer solids.

These results are consistent with the behaviour of the unremediated BTEX plume described in Chapter III. Advection of oxygen past the sorbed BTEX did not enhance removal from the slug rear. Instead, it was concluded that mass removal occurred uniformly and retardation factors calculated from centre of mass movement were similar to theoretical predictions.

4.1.6 Biodegradation Kinetics

The kinetic parameters varied in the uniform flow simulations are the maximum utilization rate, k, and the half utilization constant, K_s. The values of k= 0.493 1/day and K_s= 654.6 ug/L represent the base case values for toluene obtained from the laboratory column experiment described by MacQuarrie et al. (in submission). Increasing the maximum utilization rate, k, and decreasing K_s effectively makes the organic solute easier to biodegrade. The results obtained for an organic that is more (k= 4.928, K_s= 65.5) and less (k= 0.049, K_s= 6545.8) amenable to biodegradation than the base case are given in Figure 4.10. When k is increased by an order of magnitude and K_s decreased by the same amount, the mass loss with time is essentially the same as that obtained for the base case simulation. This implies that the biodegradation kinetics of easily degraded organics do not control the mass loss rates observed in a groundwater setting similiar to that used here. Rather, it is the rate of advective transport and dispersive mixing of the organic and the dissolved oxygen and the sorption of the organic which have a greater influence on the actual mass loss by biodegradation. Most aromatic hydrocarbons and compounds of similiar structure have kinetic constants in the range of those of the base case and those of the more easily degraded case shown in Figure 4.10. Because of the lack of sensitivity of organic mass loss to the kinetic parameters for easily degraded organics, it is implied that these rate constants need not be known precisely for such compounds.

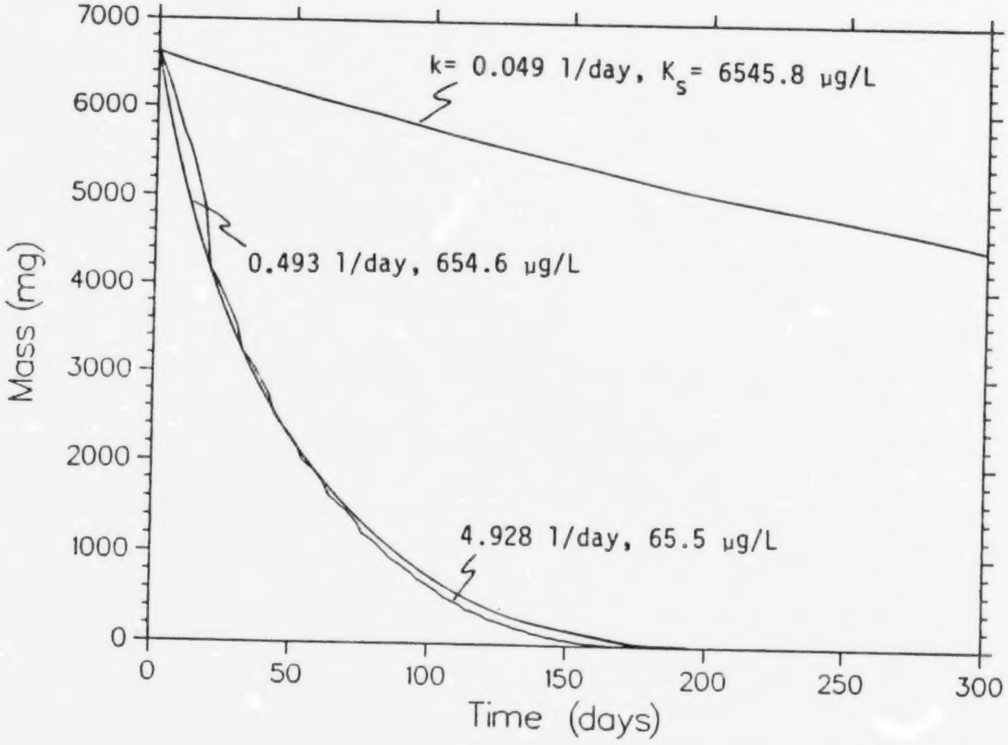


Figure 4.10: Model Prediction of Organic Plume Mass versus Time for Three Combinations of the Kinetic Constants k and K_S.

The simulation where k= 0.049 1/day and K_S= 6545.8 ug/L represents the case of a difficult-to-biodegrade organic and illustrates that, for these types of compounds, the kinetics of the biological reaction have a strong influence on the mass loss of the organic plume.

4.2 ORGANIC PLUME BEHAVIOUR IN RANDOM FLOW FIELDS

The results presented in the previous section presumed a uniform horizontal flow field in a homogeneous aquifer and that the longitudinal dispersivity could be considered a constant characteristic property of the porous medium. The use of a large constant dispersivity is a common approach taken to represent the dispersive effects caused by velocity variations below the modelling scale. Detailed natural-gradient tracer experiments, micro-scale numerical modelling studies and stochastic theory developed for flow and transport in heterogeneous aquifer materials have nevertheless demonstrated that the apparent dispersivity of a conservative solute plume will increase during the earily stages of transport (Sudicky et al., 1983; Sudicky, 1983, Sudicky, 1986; Schellenberg, 1987; Dagan, 1982). However, as a conservative solute spreads with travel time and distance such that it occupies a large volume of an aquifer, the dispersivity tends to an asymptotic value referred to as the macrodispersivity. Once this condition is attained, it has been shown that the heterogeneous medium can be replaced with an equivalent homogeneous medium characterizied by an effective hydraulic conductivity and a macrodispersivity. Mean plume behaviour in the homogeneous aquifer will closely resemble that in the actual heterogeneous one (Schellenberg, 1987). It is not known if the migration of organic solute plumes undergoing natural aerobic biodegradation is significantly affected by geologic heterogeneties or if an asymptotic mean plume behaviour can be defined. In this section, some of the features exhibited by organic plumes as they are transported through complex-structured geologic materials are demonstrated.

The hydraulic conductivity fields used here as input to the groundwater flow equation are assumed to be stationary and log-normally distributed, with point-to-point hydraulic conductivities being locally isotropic. The statistical parameters used to describe the structure of the heterogeneity and their estimated values (Sudicky, 1986) for the Borden aquifer are given in Table 4.2.

Table 4.2: Statistical Aquifer Parameters

PARAMETER	VALUE	RANGE
Log transformed hydraulic conductivity		
mean	-4.63	--
variance	0.27	0.00,1.04
Isotropic horizontal correlation length (m)	2.8	--
Isotropic vertical correlation length (m)	0.12	--
Effective hydraulic conductivity (m/day)		
horizontal	7.08	--
vertical	5.47	--

4.2.1 The Borden Case

The random hydraulic conductivity and resulting steady-state flow fields were generated using the Borden statistical parameters. The medium possesses a lenticular structure with predominately horizontal, discontinuous beds. The resulting flow lines are tortuous with regions of converging and diverging flow (Figure 4.11). Areas where the flow lines are closely spaced indicates a high velocity region and a corresponding high hydraulic conductivity bed. The average linear groundwater velocity for the generated flow field is 0.09 m/day and the maximum and minimum velocities are 0.45 m/day and 0.01 m/day, respectively.

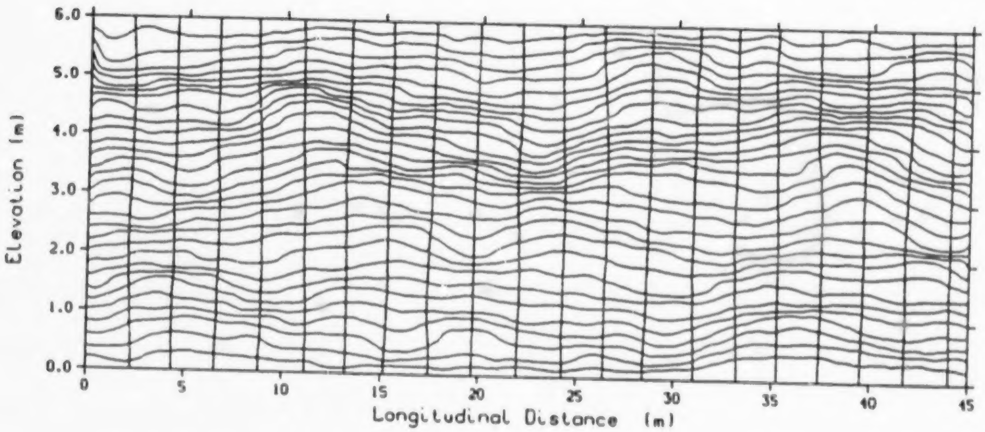


Figure 4.11: Resulting flow net generated using Borden aquifer hydraulic conductivity statistical parameters.

The transport parameters used for the simulations in the random flow fields are identical to those used in the homogeneous base case described previously, except that local-scale dispersivities are used as input along with the high-resolution nonuniform velocity field. The local-scale dispersion coefficients represent the spreading of a solute due to molecular diffusion and the tortuous flow paths caused by pore structure within an individual bed. Thus, the use of local-scale dispersivities on the order of a few centimeters or less is required to realistically depict the dispersion process in a heterogeneous medium.

Figure 4.12 shows simulated snapshots of the organic plume and dissolved oxygen distributions at various times after the slug injection. At 50 days the organic plume is very irregular with two distinct areas of high concentration. The top and middle portions of the plume are moving forward in high velocity regions. The dissolved oxygen distribution at 50 days shows an area of oxygen depletion which closely corresponds to the position of the organic plume. This consumption of oxygen within a zone encompassing a dissolved organic plume and irregularly-shaped organic and oxygen distributions have been observed in the field experiments.

By 250 days the organic plume has spread longitudinally and narrowed in the vertical direction with peak concentration values decreasing to about 203 ug/L from the initial concentration of 3000 ug/L. The narrowing in the vertical direction is consistent with the results of the field experiment (Figures 3.16 and 3.17). By comparing the orientation of the plume at 250 days with the streamlines in the flownet at that position, it is seen that the plume is in an area of upward-slanted streamlines. After 300 days, the organic plume has significantly decreased in size and the maximum concentration has been reduced to 5.6 ug/L. The zone of oxygen consumption expands with time in a manner similiar to that of a conservative solute such as chloride. The D.O. distributions shown in Figures 3.16 and 3.17 also expanded with time, however, the low D.O. zone following the BTEX slugs was considerably more extensive than that in front. Such a distribution was not developed during the simulations and was previously attributed to the presence and biodegradation of more retarded gasoline constituents. This model considers only one organic solute and so its results do not adequately represent the field experiment.

At 50 and 150 days, dissolved oxygen is completely consumed by biodegradation in the regions of highest organic concentrations; however, after 300 days the minimum dissolved oxygen concentration increases to 144 ug/L. Oxygen is able to diffuse into the interior of the small organic plume by 300 days because the organic concentrations are considerably reduced at this time such that a lower amount of dissolved oxygen is required for biodegradation. This is in turn a response to a reduced rate of biomass growth due to limited substrate availibility.

This modelling indicates, as did the simulations in uniform fields, that oxygen transport by diffusion from the unsaturated zone is not significant enough to enhance biodegradation of dissolved organics located more than a couple of meters below the water table in a predominately horizontally flowing groundwater system.

Figure 4.13 shows the total dissolved mass and the position of the center of mass for the organic plume as a function of time. The mass loss of the plume gradually slows with time as was observed in the uniform flow simulations and field experiments. Although the mass loss curve appears to be exponential with time, a plot of the log-transformed mass versus time curve is nonlinear indicating that mass loss cannot be represented by a first-order decay function.

The horizontal velocity calculated from Figure 4.13 reveals that the center of mass of the plume is migrating at 0.07 m/day up to about 130 days, and at 0.10 m/day from 130 days to 300 days. If a bulk retardation factor is computed using the above mean organic plume velocities and the average groundwater velocity of 0.09 m/day, apparent retardation factors of 1.3 for times up to 130 days and an unrealistic value equal to 0.9 for times after 130 days are obtained. A retardation factor less than 1.0 is physically inadmissable because individual reactive solute particles cannot in general travel faster than groundwater particles. The apparent value of $R = 0.9$ is an artifact of using the average groundwater velocity of the flow field for computing R where in fact biodegradation reduces the plume size such that the velocity of the plume is controlled more by the local-scale velocity within an individual bed. For the specific simulation performed here, the plume becomes controlled by a higher than average velocity zone within the aquifer.

The plume is decreasing in size in the vertical direction over most of the simulation indicating that biodegradation is removing mass at a rate faster than transverse dispersion can spread mass laterally. This is expected because of the typically small value of vertical transverse dispersivity used in the simulation. On the other hand, the plume continues to increase in size in the longitudinal direction at an almost constant rate. The variation in the hydraulic conductivity is apparently

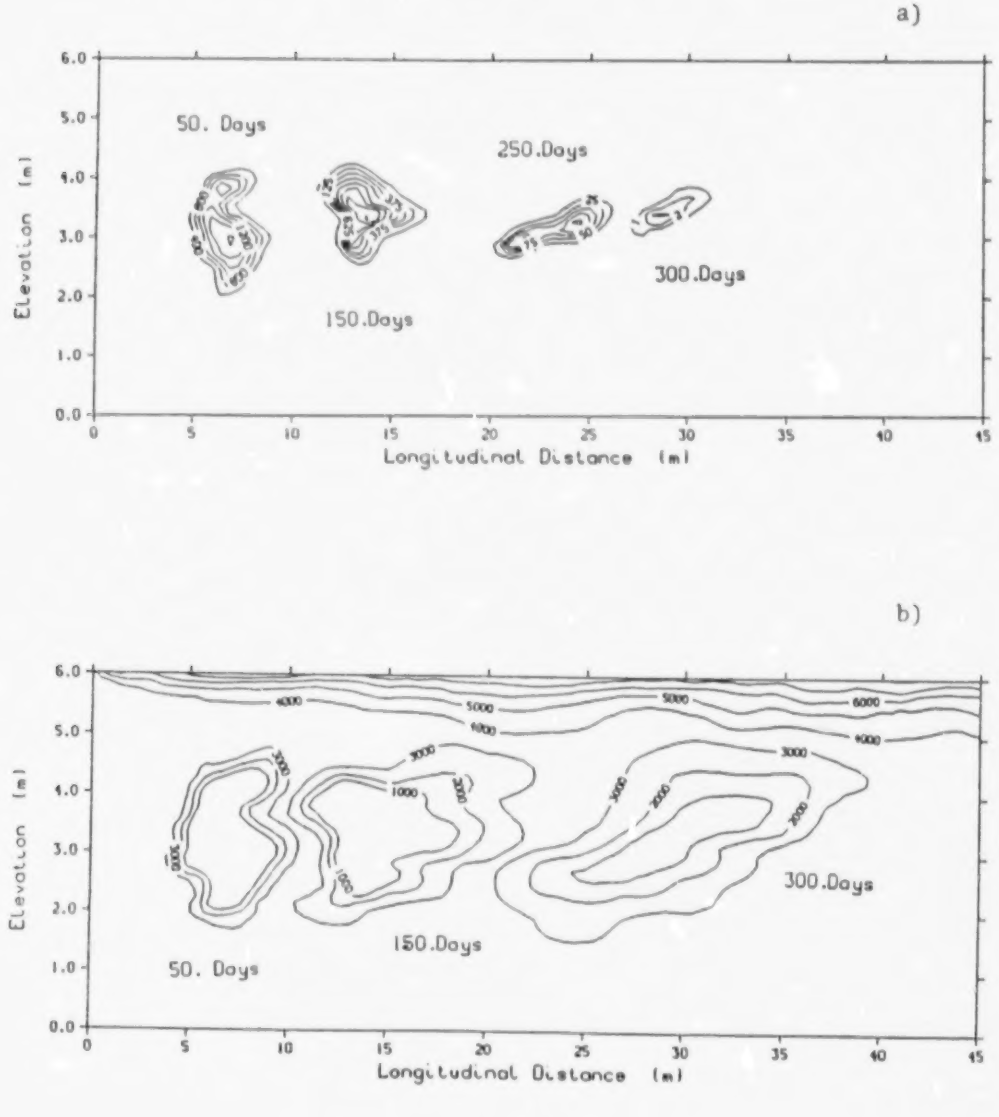
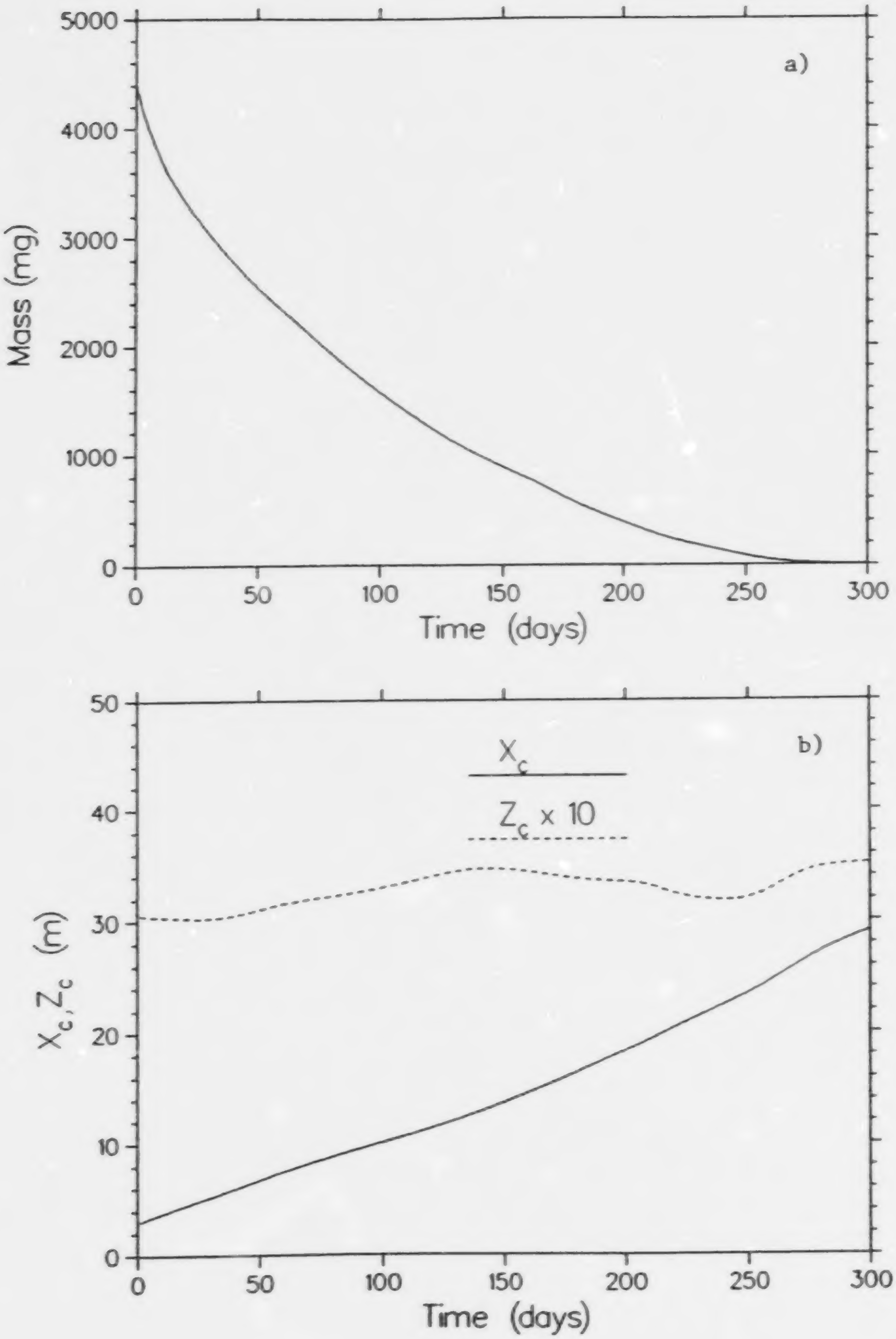


Figure 4.12: a) Dissolved Organic and b) Dissolved Oxygen Distributions for Random Flow Simulation. Concentration Isolines are in ug/L.

a more significant factor in controlling the shape of the organic plume than preferential biodegradation along the rear fringes.

Figure 4.13: **Spatial Moment versus Time Plots for Organic Plume: a) Zeroeth Moment or Mass, b) First Moment or Center of mass.**



4.2.2 Field Experiment Results, Homogeneous and Heterogeneous Modeling Cases Comparisons

A comparison of the dissolved organic mass loss curves obtained for the random flow simulation and the field benzene plume described by Patrick et al. (1986) is shown in Figure 4.14. The benzene mass at 300 days is interpolated from the mass loss curve for 0 to 406 days given by Patrick et al. (1986). Several factors prevent a rigorous comparison of model and field results. The total dissolved organic mass in the initial slug described by Patrick et al. (1986) was 13.62 g, of which only 4.25 g was dissolved benzene. The remaining dissolved components, toluene and o-, m- and p-xylene, were observed to biodegrade faster than benzene because these solutes had a smaller initial mass or injection concentration. A rigorous model and field mass comparison would require that the effects of these additional solutes be considered in the numerical simulation. Also, the kinetic parameters used as input to obtain the model mass loss curve shown in Figure 4.14 are representative of toluene. On the other hand, the initial mass and concentration of benzene injected in the field experiment and that used for the model simulation were nearly identical. Also, Patrick et al. (1986) have shown that benzene and toluene have similiar aerobic biodegradation rates in Borden aquifer material. Although the vertical two-dimensional numerical representation of the aquifer inherently neglects horizontal transverse dispersion, Sudicky (1986) has suggested that over short distances this process is relatively weak compared to longitudinal mixing in the Borden aquifer. The favourable comparison between the model prediction and the benzene mass loss is therefore encouraging considering that all the input parameters were determined independently and that no fitting of the results was attempted.

Figure 4.15 shows a comparison between the mass loss functions for the organic plume in the random flow field and that in a uniform flow field with a constant macrodispersivity of 0.81 m. The mass loss of the organic plume is greater for the latter simulation. By comparing Figure 4.15 and Figure 4.14 we clearly see that representing the mixing process with a uniform flow field and a constant macrodispersivity would not have produced as good a comparison between the field and model results. Using the macro-scale approach to account for the material heterogeneity allows far too much mixing to occur between the organic plume and the surrounding oxygenated groundwater such that mass loss is artifically enhanced. This observation has significance in practical situations where the the macro-dispersion parameters are employed in models. These parameters are then considered as constant, characteristic properties of the geologic material. However as shown in this example, using these parameters to describe the behaviour of a biodegradable organic plume could lead to significant errors in estimating the time required for remediation of the plume. This is of critical importance because the mass loss of the organic will be overpredicted if physical dispersion parameters based on conservative solute distributions are used for organic transport modelling.

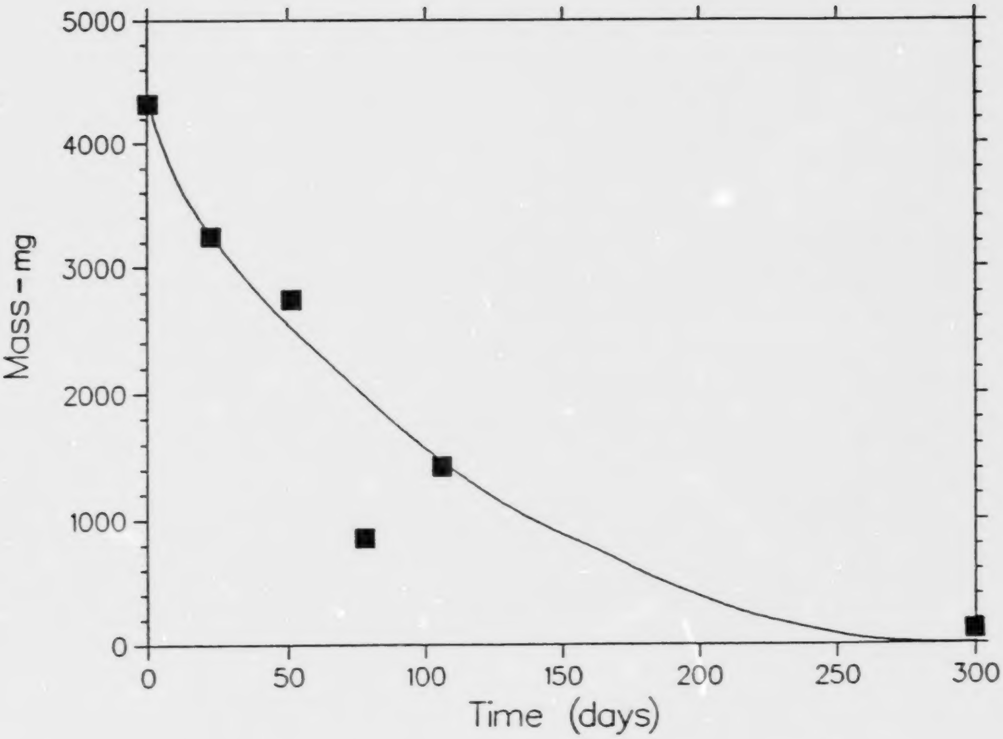


Figure 4.14: Model (line) and Field (symbol) Plume Mass Comparison. Field Data is for Dissolved Benzene as Presented by Patrick et al. (1986).

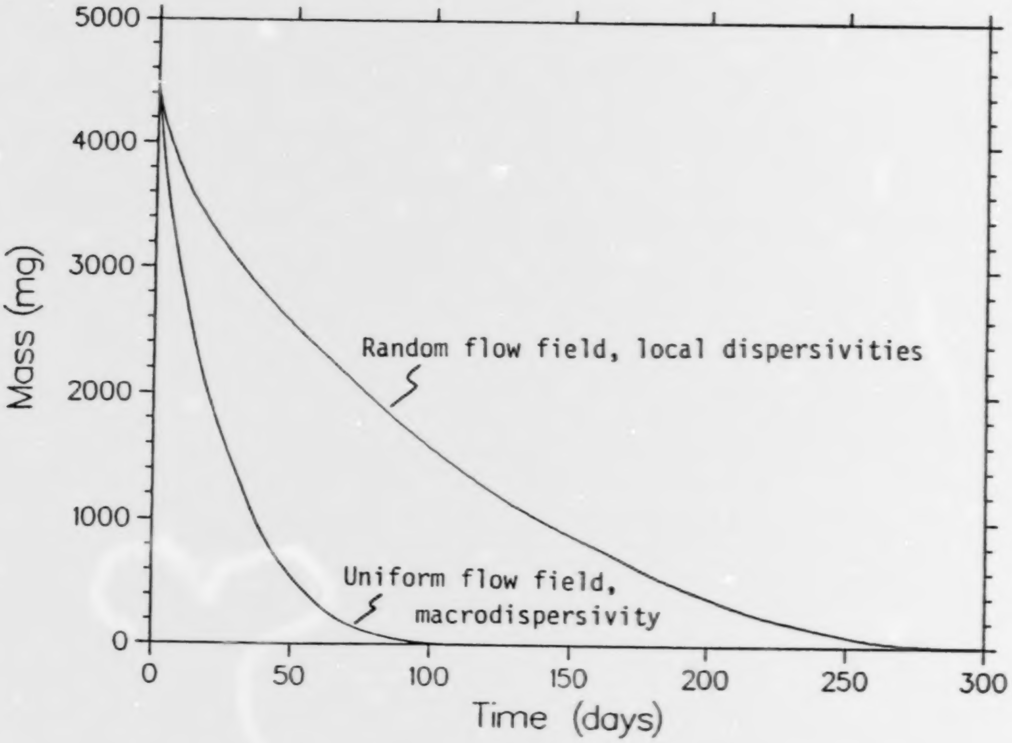


Figure 4.15: Comparison of Organic Plume Mass Loss for Different Modelling Representations of Dispersion.

4.2.3 Effects of Increased Heterogeneity

In order to investigate how the degree of aquifer heterogeneity affects mass loss of an organic plume undergoing aerobic biodegradation, a simulation was generated with the statistical properties of the previous hydraulic conductivity field, except the variance, which was increased to 1.04 from 0.27. Increasing the variance simulates a more heterogeneous medium with larger hydraulic conductivity contrasts between individual lenses. The contour of the log-transformed hydraulic conductivity field and the corresponding flow net are given in Figure 4.16. The streamlines are clearly more tortuous than those of the previous case where the variance was 0.27. The bulk average groundwater velocity is again 0.09 m/day while the maximum and minimum groundwater velocities are 1.98 m/day and 0.001 m/day, respectively.

The dissolved organic plume and dissolved oxygen distributions, shown in Figure 4.17, are much more erratic than those shown in Figure 4.12. The oxygen distribution near the water table in Figure 4.17 is the extent of downward transport at 300 days. After 250 days, the plume has split into two smaller plumes, with the

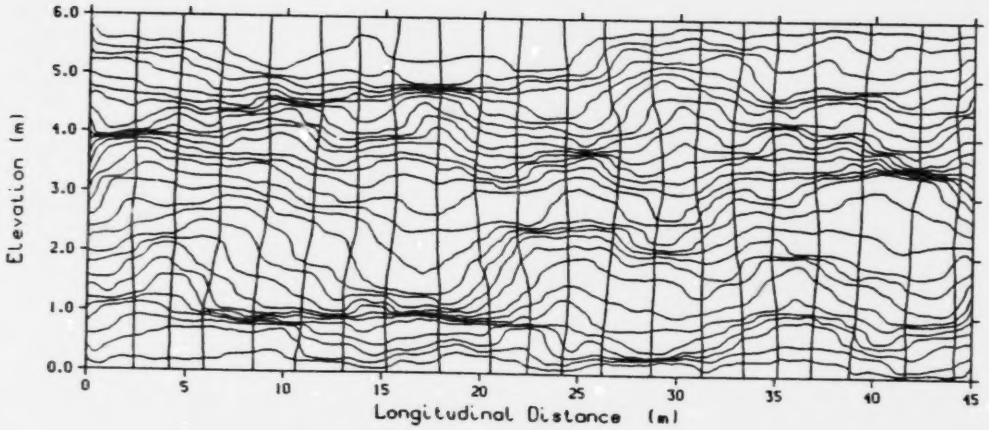


Figure 4.16: Flow net resulting from increased heterogeneity.

lower one being retained in a area of low groundwater velocity and having a maximum concentration of 107 ug/L. The corresponding areas of oxygen consumption are likewise very erratic. By 250 days, a portion of the low dissolved oxygen plume has moved far ahead of the position of the organic plume because it is nonretarded and because it has entered a high groundwater velocity zone.

The mass and the position of the center of mass versus time plots are given in Figure 4.18. Mass loss due to biodegradation is initially fast but slows with time as was the case for all previous simulations. Tailing has been noted in the results of one-dimensional transport simulations, the results of which are presented by MacQuarrie et al. (in submission). The tailing appears to be the result of mass loss rates which decrease with decreasing concentrations of the organic and dissolved oxygen. Initially, high concentrations of organic and dissolved oxygen are in contact at the fringes of the organic plume; these high concentrations result in relatively large mass losses due to rapid biodegradation. With time, biodegradation and dispersion reduce the organic concentrations while causing the zone of oxygen depletion to enlarge. Therefore, the areas where oxygen and organic are in contact, either along the plume fringes or within the plume, contain low concentrations of each solute. Biodegradation kinetics are slowed and the amount of mass available for degradation is less because of these low concentrations.

The velocity of the organic plume migrating in this random flow field is significantly different than the bulk velocity of the plume in the previous random flow simulation. Until about 125 days, the center of mass is travelling at 0.07 m/day; however, it then slows at 145 days to 0.03 m/day and remains at that velocity until 260 days. The vertical position of the center of mass has been displaced downward by almost 2 m over the 300 day simulation. This illustrates the significant effect that heterogeneties and local groundwater velocity variations can have on the position of a plume which becomes smaller with travel time.

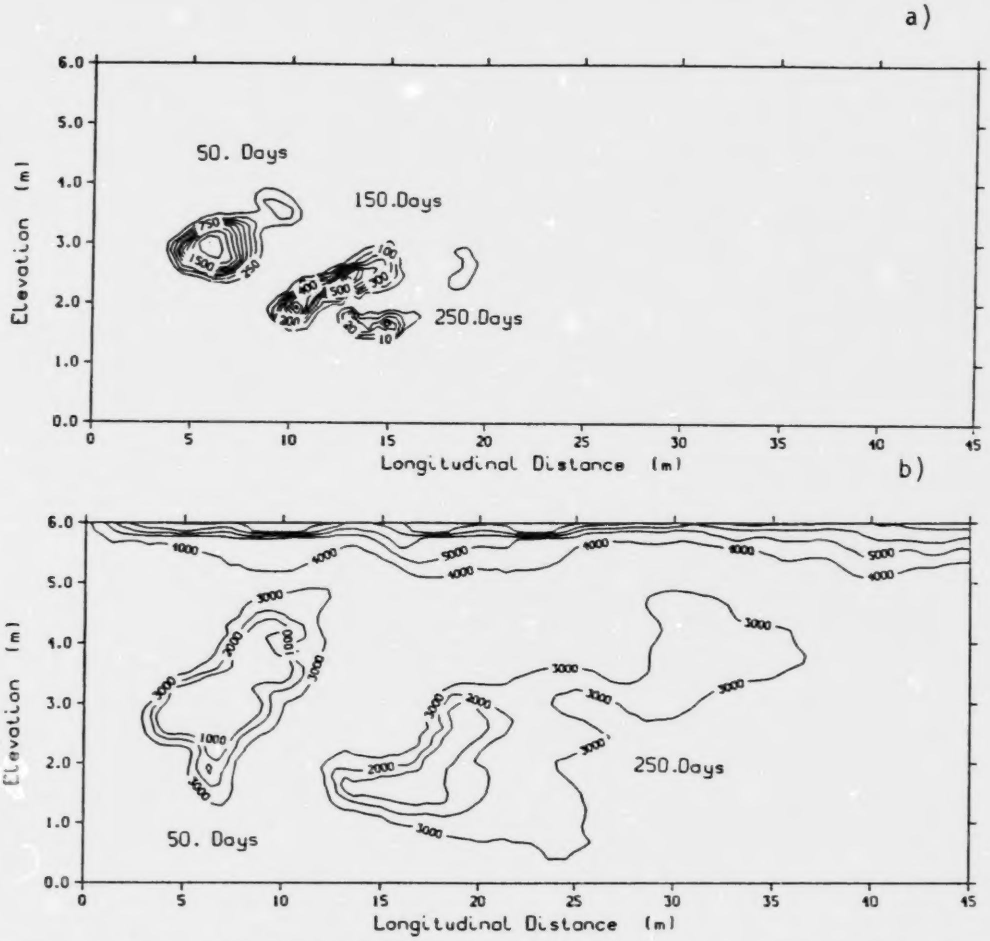
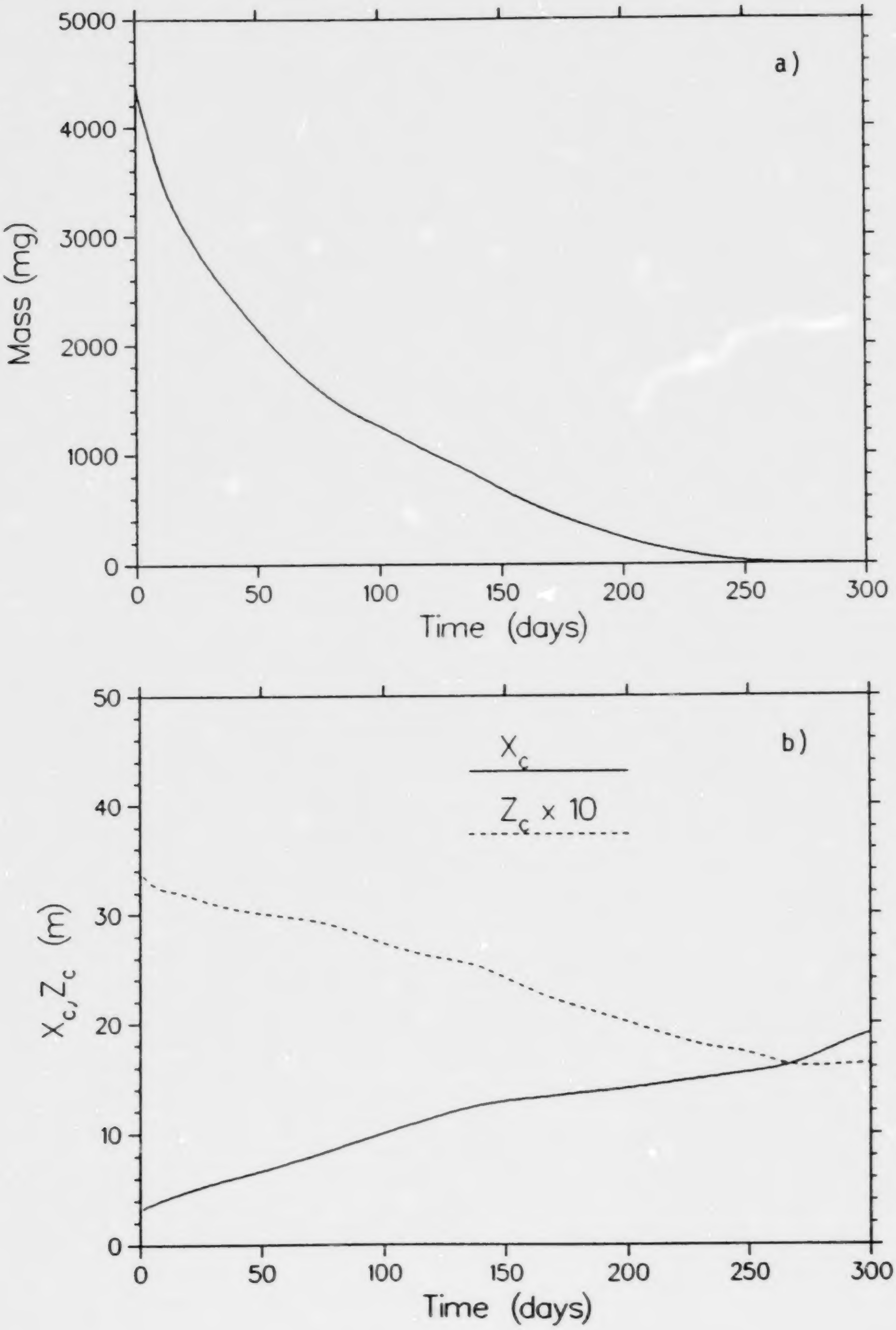


Figure 4.17: **Model Predictions of a) Dissolved Organic Plume and b) Dissolved Oxygen Distributions for increased heterogeneities.. Concentration Isolines are in ug/L.**

Figure 4.19 shows a comparison of the mass loss curves for the organic plume transported in hydraulic conductivity fields with three different hydraulic conductivity variances. The case of zero variance represents a homogeneous medium. The input dispersivities used in all cases represent the local-scale dispersivity values. As the variance is increased, the rate of mass loss increases noticeably. Because an organic plume evolves more erratically in a more heterogeneous hydraulic conductivity field, it has a larger surface area over which mixing with oxygenated groundwater can occur. It may also be the case that a high hydraulic conductivity lense may intersect the organic plume and act as an oxygen-supplying conduit. This feature is noted in Figure 4.17, where the top portion of the organic plume is quickly biodegraded because it is located in a high groundwater velocity zone.

Figure 4.18: **Moment versus Time Plots for Organic Plume with variance of 1.04: a) Mass, b) Center of mass.**



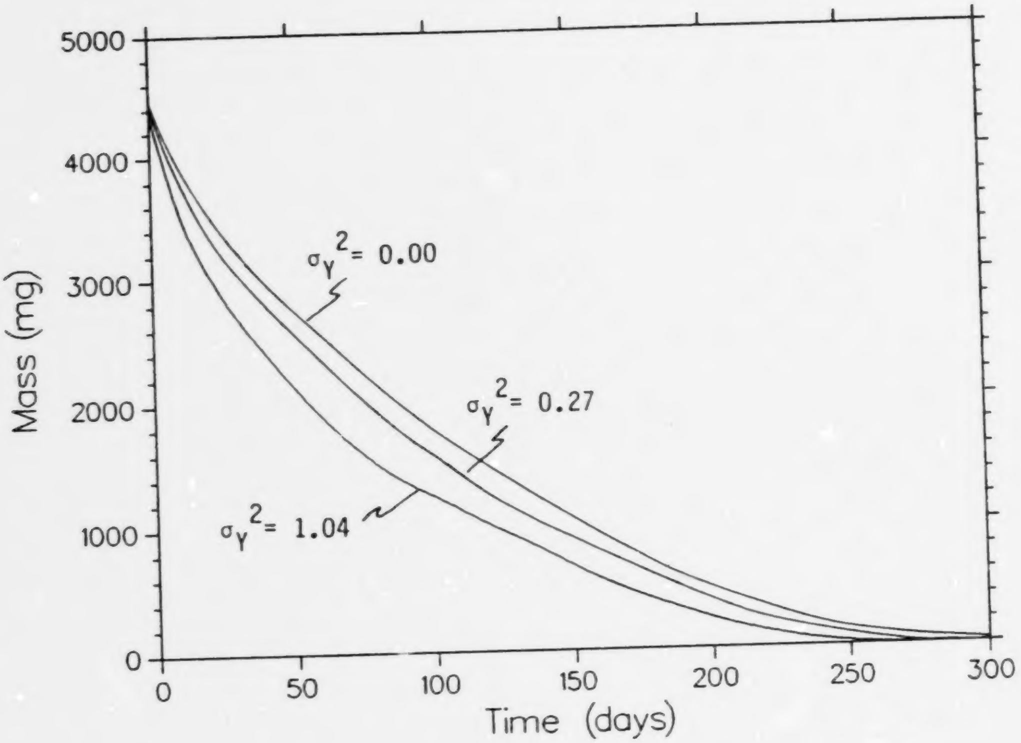


Figure 4.19: Model prediction of organic plume mass versus time for differing hydraulic conductivity variances.

4.3 CONCLUSIONS OF MODEL SENSITIVITY ANALYSIS

According to the results of the sensitivity analysis, the physical and chemical parameters of primary importance in controlling the rate of mass loss of a dissolved organic plume by aerobic biodegradation include the initial concentrations of the organic and background dissolved oxygen, the average linear groundwater velocity, the retardation factor for the organic solute and the heterogeneity of the porous medium. The rate of mass loss was observed to decrease with time because the concentrations of organic and dissolved oxygen which are in contact decrease with time due to biodegradation and dispersion. This slows biodegradation kinetics and reduces the mass of organic and oxygen mass which is available for biodegradation. When the organic concentrations in the plumes are on the order of a few ug/L, biodegradation kinetics become very slow and oxygen is able to diffuse into the interior of the organic plume.

Oxygen limitations in and around the organic plume can significantly affect mass loss. If dissolved oxygen is initially present at low concentrations or if it is rapidly consumed by a high concentration organic source, then the rate of mass loss from the organic plume is decreased. Thus, a plume eminating from a high concentration source spreads more and persists much longer than a lower initial-concentration plume.

The average linear groundwater velocity has a major effect on plume behaviour. Although a plume migrating in a high velocity flow field experiences a relatively rapid rate of mass loss because of increased mixing with oxygenated groundwater, it will also migrate a large distance downgradient. Organic plumes tend to shrink in the vertical dimension because the typically small values of transverse dispersivity cause the rate of vertical spreading to be less than the rate of mass removal by biodegradation.

The size of the initial microbial population and the biodegradation kinetic constants for easily degraded organics, such as aromatic hydrocarbons, have very little effect on organic plume behaviour, implying that these parameters need not be known precisely. However, it appears that reaction kinetics must be retained in numerical models of organic transport if a realistic representation of the interaction between biodegradation and sorption is desired. Because sorbed-phase organics are unavailable for biodegradation, sorption tends to reduce the overall mass loss with time.

The process of aerobic biodegradation causes the plume size to decrease with time such that local-scale transport parameters eventually control the behaviour of the plume. For example, the velocity of the plume will tend to reflect the groundwater velocity at the scale of individual beds while the dispersion of the plume will be controlled by the local-scale dispersivities. For the case of small to moderate sized spills it is not expected that the dispersion coefficient of a biodegradable organic plume will increase with travel time and distance in a manner similiar to a conservative solute. Thus, a macrodispersivity may not be definable for solutes undergoing oxygen-controlled biodegradation and the use of "macro" transport parameters may be inappropriate for describing organic plume behaviour. The dissolved organic and oxygen distributions were demonstrated to be very irregular in heterogeneous aquifers because of the small-scale groundwater velocity variations. As the degree of heterogeneity increases, the behaviour of the erratic organic plumes that evolve can be expected to become less predictable. This has important implications in assessing the effects of natural or artifically-enhanced remediation of contaminated aquifers in which the distribution of the hydraulic conductivity is poorly defined. Of fundamental importance to the success of such remediation projects is a comprehensive determination of the variability of aquifer structure.

Chapter V

CONCLUSIONS

Two field experiments in which gasoline compounds dissolved in water were injected below the water table and into a shallow, unconfined sand aquifer have been conducted as part of this research program. The first experiment involved the injection of only dissolved benzene, toluene, and xylenes (BTX) while the second involved the injection of gasoline-contacted water which contained a number of other gasoline consitituents in addition to benzene, toluene, ethyl benzene and xylenes (BTEX).

Results of monitoring of the BTX plume for 406 days are described in the Phase II Report (Patrick et al., 1986) and were summarized in Chapter II of this report. It was concluded that oxygen was used during the biodegradation of BTX and that BTX persisted in aquifer zones of low oxygen concentrations.. Monitoring of the BTX plume continued after 406 days to determine if biodegradation of BTX continued after BTX concentrations were reduced to about 1 ug/L. Monitoring of the BTX plume from day 406 to day 750 revealed that biotransformation of BTX does continue below 1 ug/L concentrations and therefore there is no BTX persistance threshold.

The second injection experiment was conducted to compare the field behaviour of BTEX to BTX and also to evaluate nitrate addition to oxygen deficient BTEX-containing groundwater as a remediation scheme. Two separate volumes of gasoline-contaminated groundwater were created side-by-side. One of these volumes (remediated) received an upgradient addition of nitrate-containing groundwater while the other remained unremediated. Laboratory biotransformation experiments indicated that nitrate may be used in place of oxygen during degradation of BTX in oxygen deficient environments. BTEX removal when only nitrate was present occurred extremely slowly. BTEX removal when both oxygen and nitrate were present occurred more rapidly than when oxygen alone was present. The injection and remediation was designed to test these observations in the field.

By 78 days, the non-sorbing nitrate began to overtake the retarded remediated BTEX plume. BTEX and nitrate tended to occupy the same layers within the aquifer, thus in situ mixing of the contaminant plume and remedial solutions was achieved with a minimum of hydraulic control.

After 148 days, the total BTEX mass remaining in solution was the same for both plumes. Toluene and m-xylene removal from the remediated plume was enhanced somewhat. Because the injected masses were small, most of the BTEX removal occurred aerobically. Oxygen did not become limiting at late times because of the small plume size. The error involved in calculating such small masses was large at late times, thus the effect of nitrate addition on BTEX persistence was not unequivocally demonstrated. The laboratory biotransformation experiments indicated that the addition of nitrate addition to oxygen-deficient BTEX plumes did accelerate degradation and therefore nitrate may be a valid remedial technique in an oxygen deficient aquifer.

Although the field experiment did not successfully evaluate the addition of nitrate as a remedial measure for gasoline-contaminated groundwater, the results provide insight into the fate, mobility, and persistence of BTEX under natural conditions. Retardation factors calculated for unremediated BTEX were within the range of values obtained from small-scale laboratory experiments. It was concluded that other dissolved gasoline constituents had no significant effect on the biodegradation or mobility of BTEX during early times when the plume was still relatively large. After sufficient time had passed to allow the chromatographic separation of compounds due to differing retardations and the plumes had become quite small, biodegradation, oxygen limitation and aquifer heterogeneties caused the BTEX plumes to move erratically.

A numerical model was used to simulate the transport and biodegradative interaction of toluene and dissolved oxygen in different hydrogeologic settings. A model sensitivity analysis was performed to determine the parameters having the greatest influence on the fate, persistence and mobility of BTEX. According to this model, the initial concentrations of the organic and oxygen, groundwater velocity, retardation factor for the organic and heterogeneity of the porous media have the most control on the rate of mass loss. The size of the intial microbial population and biodegradation kinetic constants need not be known precisely since they had little effect on the persistence of the organic. The use of "macro" transport parameters may be inappropriate for describing organic plume behaviour. The dissolved organic and oxygen distributions were demonstrated to be very irregular in heterogeneous aquifers because of the small-scale groundwater velocity variations. As the degree of heterogeneity increases, the behaviour of the erratic organic plumes that evolve can be expected to become less predictable. This has important implications in assessing the effects of natural or artifically-enhanced remediation of contaminated aquifers in which the distribution of the hydraulic conductivity is poorly defined. Of fundamental importance to the success of such remediation projects is a comprehensive determination of the variability of aquifer structure.

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Appendix A

DESIGN AND IMPLEMENTATION OF THE FIELD EXPERIMENT

The remediation experiment was conducted at the field site at Canada Forces Base Borden. Planning and preparation for the field experiment began in May, 1986. The injection experiment commenced on June 18, 1986. This appendix describes the design and implementation of the field experiment undertaken to evaluate nitrate addition as an insitu remedial measure for gasoline-contaminated groundwaters.

A.1 The Remediation Scheme

Injection of gasoline-contaminated water was to be followed by a remediation attempt by nitrate addition, the purpose of which was to evaluate in situ aquifer restoration processes. It was decided to inject nitrate after the gasoline contaminated water was in place instead of treating at ground surface. Addition of nitrate upgradient from the gasoline contamination would allow the unretarded nitrate could sweep through the retarded BTEX.

A simplistic numerical model was developed to assist in the design of the remedial injection experiment (Berry-Spark et al., 1986). The model simulated the simultaneous movement of benzene and nitrate as it swept through the benzene slug from the rear. The two solutes interacted in a biodegradation reaction and were removed from solution according to some biodegradation rate. Results obtained from this model suggest that if nitrate remediation occurred at the rear of a BTEX plume, mass loss would be apparent in areas of nitrate and BTEX overlap. In addition, the centre of benzene mass was displaced forward of that predicted from sorption because of the mass removal from the rear. Assuming that BTEX can be degraded during denitrification, the model simulations indicate that the resulting BTEX distributions and centre of mass locations will differ from those obtained from a similar unremediated slug.

A.2 Injection Solutions

The field experiment required the preparation of two separate injection solutions: gasoline-contaminated water and nitrate spiked water.

(a) Gasoline contaminated water - It was desirable to produce a contaminant plume which simulated water which had contacted spilled or leaked gasoline. The following criteria were the basis for the design of this solution:

1. The concentration of each aromatic constituent should be readily detectable in the laboratory at the injection composition and three orders of magnitude lower.

2. BTEX concentrations should reflect a realistic setting therefore the concentration injected should be less than saturated from a gasoline source. Also, the injected water should contain dissolved oxygen concentrations approximately equal to the dissolved oxygen content of the injection interval.

3. The concentrations should remain relatively constant during the injection.

4. BTEX concentrations and water volume should be high enough to produce noticeable mass losses by biodegradation both before and after oxygen depletion.

5. The volume injected needed to be small enough such that two slugs could be injected and migrate side by side without mutual interference and yet close enough together to remain within the domain of the sampling network.

6. The volume should be large enough to ensure that the centres of the slugs would obtain minimal oxygen replenishment.

With these constraints forming the basis of the design, it was decided to inject two volumes of 2500 L each containing approximately 3.0 mg/L total BTEX. By using groundwater obtained from the injection interval, the injection water would contain approximately the same dissolved oxygen concentration as the interval into which it was to be injected.

(b) Nitrate injection - The second injection represents the attempt to remediate the gasoline contamination. In designing this injection, the following criteria were the main focus:

1. The nitrate mass must be at least twice the nitrate demand of the BTEX and background dissolved organic carbon in the contaminant slug to ensure adequate nitrate for complete breakdown of BTEX during denitrification. The nitrate mass must also be large enough to accomodate nitrate losses as a result of assimilation.

2. The dissolved oxygen concentration must be approximately equal to the dissolved oxygen content of the injection interval so that that denitrifying conditions may develop fairly rapidly.

3. The volume injected must be sufficiently large enough to allow adequate time for biodegradation during the overlap of contaminated water and nitrate containing water.

4. The volume injected and injection interval must allow complete encompassment of the BTEX slugs.

In light of these criteria, it was decided to inject 2500 L of water containing 107.8 g of nitrogen as potassium nitrate and 4.8 kg of chloride as sodium chloride. Although this nitrate mass largely exceeded the nitrate demand of the BTEX alone, it was necessary to use this much nitrate in order to ensure sufficient available nitrate in overlapping nitrate - BTEX slugs. The nitrate demand of the BTEX slug represents only 5% of this amount so a nitrate loss due to utilization during BTEX biodegradation would be difficult to detect. Chloride was added as a conservative tracer in order to determine the potential migration of the nitrate since the transport of nitrate could have been affected by its involvement in biochemical reactions.

A.3 Injection Geometry and Wells

Previous problems encountered during the injection of a solution containing BTX were water table mounding and the length of time required to inject the solution (Patrick, pers. commun.). These problems were alleviated through the use of more than one injection well per slug.

Gasoline contaminated groundwater was injected through the four wells (Figure 4.1.) constructed with 32 mm O.D. PVC pipe fitted with a 0.61 m threaded No. 10 commercial well screen (Timco). The grouping of these wells allowed the simultaneous injection of two spherical 2500 litre BTEX slugs. The wells were installed in May, 1986 by a jetting-of-casing method (Cherry et al., 1983, Mackay et al., 1986b) using a Cobra percussion hammer and native groundwater to a depth of 2.9 m. 0.50 m of casing was left extending above the ground.

Nitrate and chloride spiked groundwater was introduced through the four wells (Figure 4.1) which allowed injection of an ovoid slug of water centred 1.5 metres upgradient from one BTEX slug. It was anticipated that nitrate and chloride would travel at groundwater velocity and overtake BTEX in about 175 days, ensuring adequate time for the remediated BTEX slug to become oxygen depleted. It was decided to inject unmodified groundwater behind the unremediated BTEX slug in order to treat both slugs the same hydraulically.

The eight injection wells used for the second injection were were constructed of 38 mm I.D. PVC pipe, capped at the bottom and slotted with a hacksaw over a depth interval of 2.0 to 3.6 m. Nitex nylon screening was wrapped and secured over the slotted section. Installation of these wells was done in May, 1986 by percussion drill rig by pounding a steel casing with a PVC tip by to the required depth. The injection well was inserted and only the steel casing was withdrawn, allowing the cohesionless sand to collapse around the well. Forty-eight hours prior to the initial injection, all injection wells were developed by pumping for approximately 5 minutes until clear water was yielded.

A.4 Injection System

The injection system was designed after similar systems described by Mackay et al. (1986b) and Patrick et al. (1985). Although several criteria were imposed during the design of the system, the most important are outline here. The injection system was designed to:

1. be versatile, allowing delivery of 5000 L to 4 injections wells at 1.5 L/min on day 1 and 4800 L to 8 injection wells at 0.75 L/min per well on day 3

2. allow the preparation of spike solutions on site and dilution of these spikes in line en route to the injection wells

3. be simplistic, allowing quick disassembly and reassembly between injections, adaptable to both injection types

4. have individual well flow rate controls and flow meters

5. allow sampling of injection water immediately prior to injection

6. limit the exposure of the water to the atmosphere so as to minimize volatilization of the aromatic hydrocarbons and oxygenation of the injection solutions

The final designs of the injection systems are shown in Figures A.1 and A.2. Both systems employed the same basic design with modifications made to accomodate spike solution preparation. In general, water was pumped from a reservoir to prepare a solute spike solution. Water was also pumped from the reservoir to be mixed in line with the spike solution. After addition of the spike solution, the line was split and four wells were injected simultaneously. A split in the line before the spike addition allowed injection of unmodified groundwater.

A spike solution of gasoline-contaminated water was obtained by passing water and unleaded gasoline at predetermined flow rates through a mixing vessel. The mixture then passed to a settling vessel where the two immiscible fluids were allowed to separate. Water containing soluble gasoline constituents at approximatedly seven times the injection concentration was withdrawn from the bottom of this settling vessel. The 'gasoline saturator' was designed, callibrated and tested in the laboratory prior to field use. The gasoline used during laboratory callibration was not used for the field experiment so the spike solution was less concentrated. The resultant injection water contained approximatedly 0.8 mg/L total BTEX instead of the intended 3.0 mg/L.

The nitrate and chloride spike solution system consisted of three 200 L drums lined with collapsible polyethylene bags. The spike solution was prepared by adding pre-weighed sodium chloride and potassium nitrate to 200 litres of groundwater obtained from the 2000 litre reservoir. A shaft mounted propellor was used to stir the solution containing nitrate and chloride concentrations approximately four times the concentration of the injection solution.

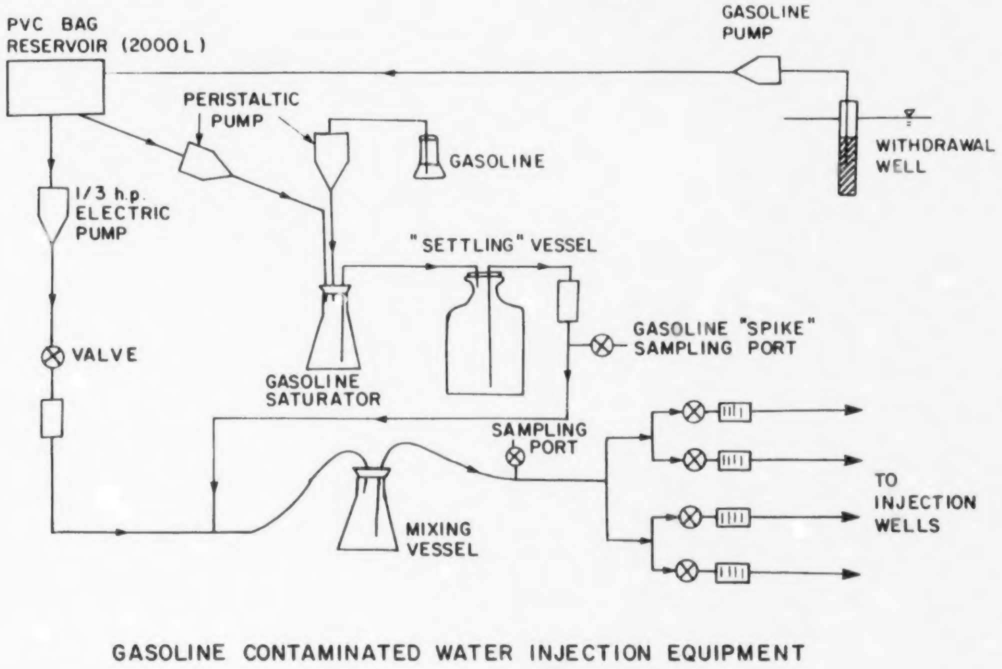
PVC BAG
RESERVOIR (2000 L)
GASOLINE
PUMP
PERISTALTIC
PUMP
GASOLINE
WITHDRAWAL
WELL
1/3 h.p.
ELECTRIC
PUMP
"SETTLING" VESSEL
GASOLINE "SPIKE"
SAMPLING PORT
VALVE
GASOLINE
SATURATOR
SAMPLING
PORT
TO
INJECTION
WELLS
MIXING
VESSEL
GASOLINE CONTAMINATED WATER INJECTION EQUIPMENT

Figure A.1: Schematic of the gasoline-contaminated water injection apparatus

Due to the logistical problems involved in storing thousands of litres of water above ground prior to the injection, a well approximatedly 100 m down gradient from the injection wells was pumped while the injection was occurring. A 2000 L collapsible PVC bag acted as a temporary water reservoir during the injection. Using the method of Neuman (1975) for the calculation of water table drawdown

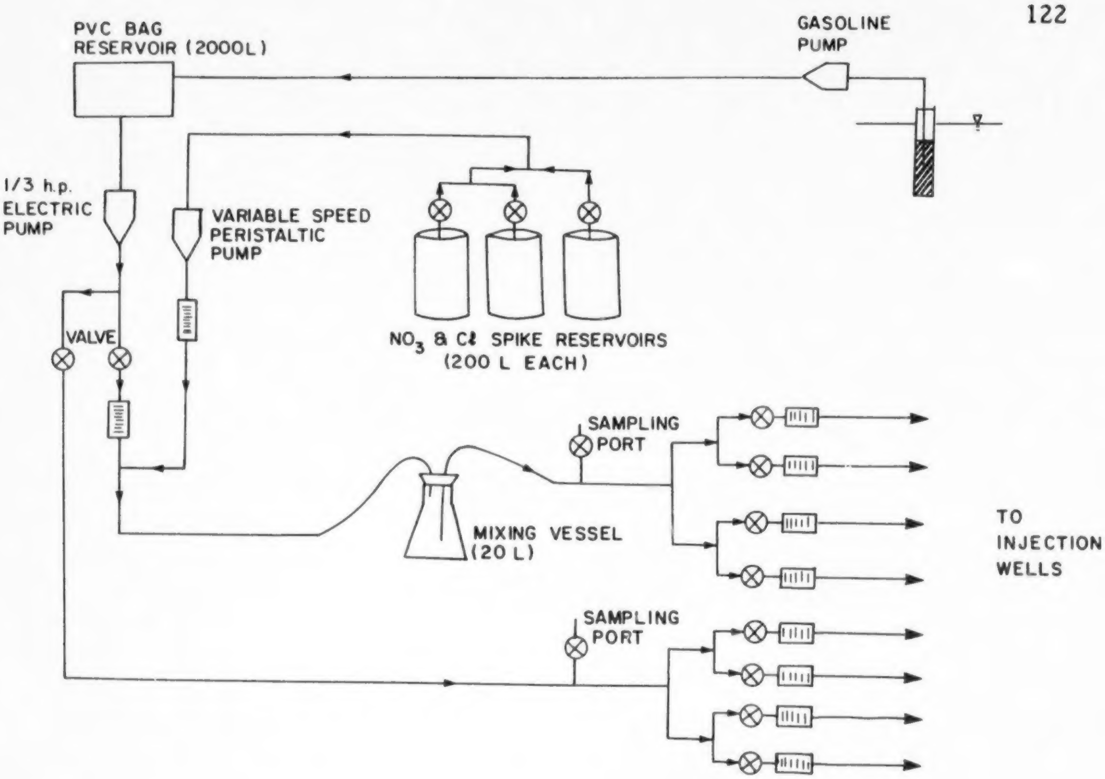
PVC BAG
RESERVOIR (2000L)
GASOLINE
PUMP
1/3 h.p.
ELECTRIC
PUMP
VARIABLE SPEED
PERISTALTIC
PUMP
VALVE
NO$_3$ & Cl SPIKE RESERVOIRS
(200 L EACH)
SAMPLING
PORT
MIXING VESSEL
(20 L)
TO
INJECTION
WELLS
SAMPLING
PORT

Figure A.2: Schematic of the nitrate and chlorde spiked water injection apparatus

in an unconfined aquifer, the maximum effect of continuous pumping of this well was estimated at the injection wells to be on the the order of 10^{-4}m. It was assumed that periodic pumping of this well during the injection would not affect the hydraulics of the injection.

Segments of the injection system were tested in the laboratory in order to callibrate the flow meters and check for leaks. The entire injection system was assembled in the laboratory and tested for compatibility prior to the injections. After arrival at the Borden site on June 16, 1986, the gasoline injection system was assembled and a trial injection without gasoline was performed for a half hour so that flow meters and pumps could be adjusted and to ensure that the injection wells could dissipate the required flow rates.

A.5 Monitoring Network

The network consisted of the original teflon bundle piezometers installed for the Stanford University and University of Waterloo experiment (Mackay et al., 1986b) and piezometers installed later (Patrick et al., 1985). The piezometer grid density varied from 0.25 m at the injection wells to 3.0 m at a distance of 15.5 m down gradient from the injection wells.

Each original Stanford multilevel piezometer consisted of 12 to 20 3.2 mm O.D. teflon tubes spaced vertically at regular intervals from depths of about 1.8 to 5.4 m. The vertical spacing between sampling points was usually 0.20 m and occaisionally 0.30 m. The multilevel peizometer design is discussed in more detail by Mackay et al. (1986b) and is based on a design originally described by Cherry et al. (1983).

Piezometers installed in 1984 were similar to the Stanford multilevel samplers but polyethylene tubing was used in place of teflon. These piezometers consisted of 23 sampling points spaced at 0.20 m vertical intervals from a depth of about 0.50 m to 4.8 m.

Several of the teflon piezometers were pulled out, washed, repaired and re-installed by percussion drill rig five weeks prior to the injection. Many of these piezometers were pulled out again and re-installed by the jetting-of-casing method in October, 1986 in response to the horizontal movement of the tracer slugs. Installation occurred at least six weeks prior to the arrival the contaminant slugs and was follwed by pumping for about 5 minutes for development.

A.6 The Field Injection

The 2000 L PVC bag was filled with groundwater 10 hours before the injection commenced. The injection of gasoline-contaminated water began at 10:00 a.m. on June 18, 1986 and continued for 13.9 hours. The injection rates remained remarkably constant at each well at 1.5 L/min and a total of 5000 L was injected.

During the first injection, samples of both the spike solution and the injection water were obtained in sealed hypovials approximately half-hourly. Samples were obtained hourly from four nearby piezometers using the sampling manifold. Samples were store in coolers on cold packs and after thirty-six hours, were transported to the University of Waterloo for analysis of BTEX.

Dissolved oxygen and temperature measurements were made in the field on the injection water half-hourly and on water obtained from several piezometers in the vacinity of the injection wells. Water level measurements were obtained from the injection wells and nearby wells, indicating that the hydraulic heads increased about 3 cm very gradually over the duration of the injection and dissipated within a 1.5 m radius from the injection wells. Water levels returned to initial conditions within an hour after cessation of the injection.

As soon as the injection was completed, the four injection wells were manually pulled out to ensure that no water remained behind in the stand pipes of the injection wells. The gasoline-contaminated slugs entered the aquifer as a uniform pulse.

The following day, the injection system was removed from the site and flushed with the water remaining in the PVC bag. The second injection system was set up on June 21, 1986 and tested without injecting.

Injection of the nitrate and chloride commenced on June 22, 1986 at 8:30 a.m. and continued for 13.3 hours. During the injection, one of the wells receiving unmodified groundwater began to overflow and it was thought that the standpipe was plugged by a rodent carcass. Flow to the wells adjacent was increased in order to compensate for the plugged well. The flow rate remained fairly constant at about 0.75 L/min at each well receiving nitrate. A total of 4800 L of water was injected below the water table although only 2400 L contained the nitrate and chloride tracers. Miscalculations in the field stopped the injection short of the injection target of 5000 L.

During the second injection, samples of the nitrate/chloride spike solution and both the unmodified and remedial injection solutions were obtained approximately every 1.5 hours, stored on cold packs in coolers, and later transported to the University of Waterloo for chloride and nitrate analyses. Similarly, samples of both injection solutions were obtained every three hours for BTEX analysis to ensure that desorption of BTEX from the injection equipment was minimal.

Hourly dissolved oxygen measurements were made in the field using both injection waters and water obtained from four piezometers at varying radial distances from the injection wells. The temperature of the injection solutions was monitored hourly for the first 4 hours.

Water levels were measured periodically at four nearby wells over the course of the injection, indicating that the maximum increase in hydraulic head was 0.15 m.

Upon completion of the injection, all eight injection wells were jacked out of the ground for reasons previously described.

A.7 Results of Injection Sampling

Figure A.3 shows the dissolved oxygen and BTEX concentrations and temperature trends for the BTEX injection solution. Average concentrations and temperature are listed on the figure. BTEX and D.O. masses were obtained by integrating the concentration functions with respect to time.

BTEX concentration ranged from 0.5 to 1.1 mg/L during the injection. This fluctuation is likely due to variation in the rate at which gasoline was pumped into the gasoline saturator. Dissolved oxygen concentrations decreased during the initial two hours possibly because of increasing water temperature. The injection water warmed considerably during storage in the PVC reservoir.

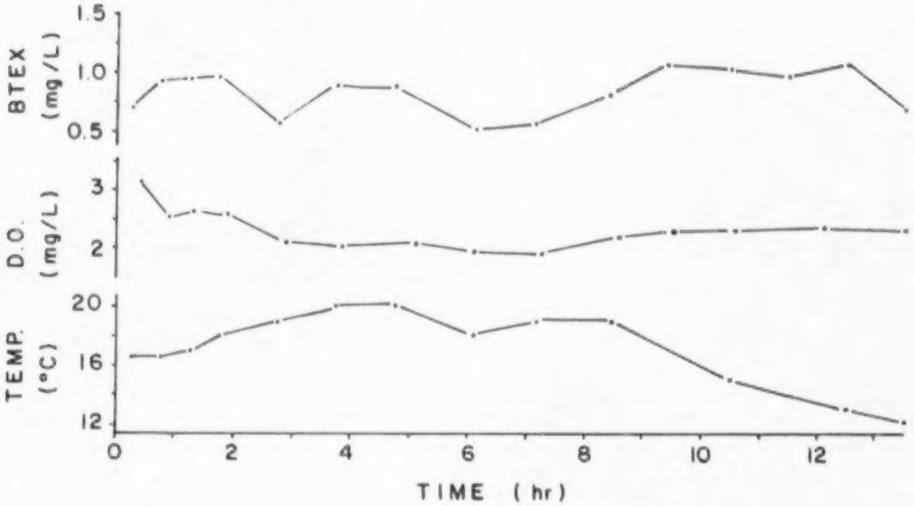

Figure A.3 Concentration of solutes and temperature of the gasoline contaminated injection water

Figure A.4 shows the time depandant nitrate, chloride, and D.O. concentrations of the nitrate/chloride injection solution. Although the source of groundwater used for preparation of the initial injection was also used for preparation of the this injection, the average D.O. concentration was slightly higher presumably because of the lower average temperature. Nitrate and chloride masses were determined by weighing the dry chemicals before addition to the injection solution.

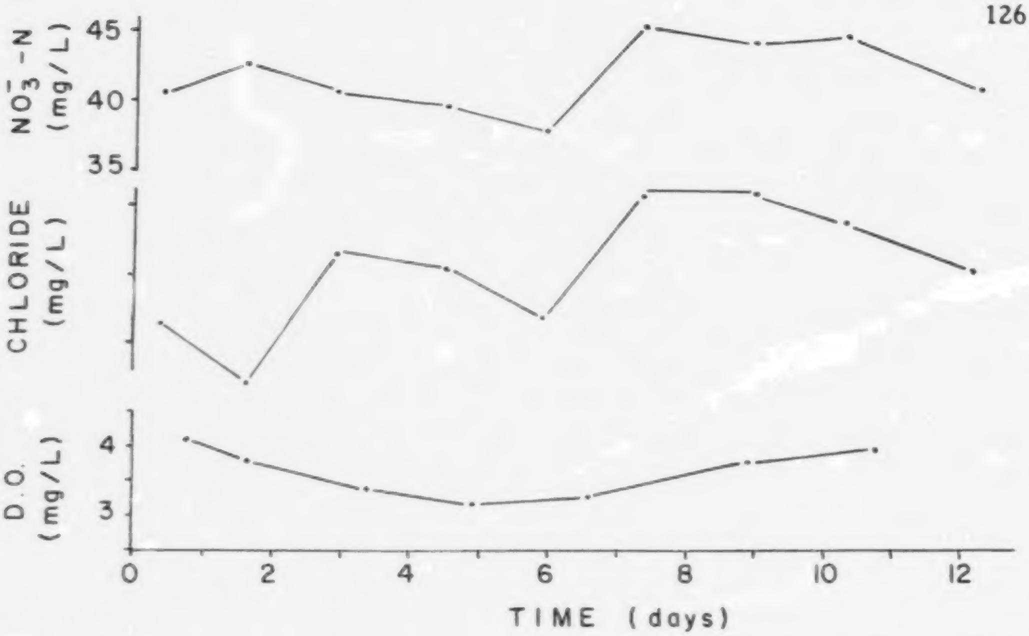

Figure A.4: Concentration of solutes in nitrate/chloride spiked injection solution

A.8 References

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Appendix B

ANALYTICAL METHODS

Water samples were collected in both the field and from laboratory experiments. Collection of samples from the field site resulted in 500 to 1000 samples per month on which BTEX, nitrate and chloride analyses needed to be performed as quickly as possible. This necessitated using rapid analytical techniques. Samples collected from laboratory experiments, although much fewer in number, were analyzed using these same techniques.

B.1 BTEX

Samples to be analyzed for BTEX were usually collected in 18 cm^3 glass hypovials and capped with teflon faced silica septa. BTEX concentrations were measured using a solvent extraction technique followed by solvent analyses using gas chromatography. This micro-extraction technique used is described in more detail in Patrick et al. (1985). Extraction solvent to sample water volume ratios were altered somewhat after the first two sampling sessions in order to decrease the detection limit. A Hewlett-Packard gas chromatograph (model 5890) and two Schimadzu gas chromatographs, all equipped with flame ionization detectors and electronic integrators, were used simultaneously to analyze solvent from the field samples. All laboratory samples were analyzed using the Schimadzu 2 gas chromatograph. Although BTEX eluded from the gas chromatograph capillary column in five minutes, sample run times were ten minutes to allow the passage of all gasoline constituents through the column. All extractions and gas chromatograph injections were performed manually.

To ensure the quality of the concentration data, standards of BTEX compounds were prepared and extracted in hypovials and run every 10 to 15 samples on the gas chromatographs. The concentration of BTEX in the standards was decreased about every two sampling sessions to correspond with the decreasing concentrations observed in the field samples or was adusted to approximate the concentrations expected in the laboratory experiments.

Method detection limits (M.D.L.) for BTEX are given in detail in Table B.1 but were in general less than 1 ug/L. Method detection limits were determined by the procedure recommended by USEPA/EMSL. The M.D.L. is defined as the minimum concentration measurable with 99% confidence that it is greater than zero (USEPA, 1982a). The relative error is also listed in Table B.1. Because of the high error obtained for the Hewlett Packard gas chromatograph (HP5890), samples found to contain BTEX were often re-analyzed using one of the Schimadzu units.

Table B.1: Method Detection Limits for BTEX (18 cm^3 sample size)

COMPOUND	GAS CHROMATOGRAPH	S%	X	X_o	E%	MDL
BENZENE	Schim 1	8.42	1.72	1.84	-6.69	0.44
	Schim 2	10.35	1.77	1.84	-4.28	0.55
	HP5890	9.74	2.94	1.84	59.23	0.86
TOLUENE	Shim 1	6.38	1.83	1.84	-0.12	0.35
	Shim 2	19.07	1.25	1.84	-31.94	0.71
	HP5890	8.87	2.69	1.84	46.68	0.72
ETHYL BENZENE	Shim 1	12.17	2.22	1.90	12.17	0.81
	Shim 2	21.52	2.13	1.90	12.11	1.38
	HP5890	37.77	2.74	1.90	44.14	3.11
P-XYLENE	Shim 1	15.49	1.84	1.89	-2.92	0.85
	Shim 2	6.91	1.86	1.89	-1.53	0.39
	HP5890	36.92	2.13	1.89	12.76	2.36
M-XYLENE	Shim 1	16.23	2.06	1.87	10.14	1.00
	Shim 2	7.21	2.07	1.87	10.65	0.45
	HP5890	29.87	2.85	1.87	52.48	2.55
O-XYLENE	Shim 1	14.53	1.70	1.93	-11.88	0.74
	Shim 2	5.89	1.67	1.93	-13.09	0.30
	HP5890	44.06	1.85	1.93	-4.13	2.44

S% = relative standard deviation
X = mean of replicate determinations
Xo = true value
E% = relative error
MDL= method detection limit

B.2 Low Level BTEX Analyses by Purge and Trap GCMS

Samples were concentrated by a purge and trap technique using an Evirochem Universal Concentrator (model 810N with 20 ml purge vessels with septum ports) and quantitatively analyzed using a Hewlett-Packard gas chromatograph (model 5890 with a standard 30 m DBWAX capillary column) coupled with a Hewlett-Packard mass selective detector (model 5970).

Normally, 20 ml samples are analyzed by purge and trap, however, only 10 ml sample voluems were availabe for the first two sampling 1986 sessions. These samples were made up to volume (20 ml) with organic free reagent water to keepo the purging effeciencies uniform. The purge vessel was installed and brought in line with the initial trap prior to sample introduction to prevent losses due to volatilization. A sample was transferred from the volumetric flask or bottle via a glass syringe. Injecting through the purge vessel septum. The helium puge time was 11 minutes followed by a 5 minute trap 1 dehydration and then a trap to trap transfer time of approximately 3 minutes. The GC run was under 5 minutes. BTEX were monitored by mass spectrometry selective ion monitoring (SIM).

Two independant methanolic stock standards were prepared as previously described (Patrick et al., 1985). These were diluted by accurately injecting into 100 ml aliquots of reagent water in volumetric flasks with septum caps. One solution was used to calibrate the analytical system, the other was used as an on going check on performance. Reagent water blank runs were performed periodically as well. A given 100 ml volume of standard was used only once. Approximately 3 ul of a methanolic p-fluorotoluene internal standard solution was accurately injected into the purge vessel prior to starting the run and the internal standard amount value adjusted accordingly.

All glassware was soaked briefly in hot alkaline cleaning solution, then rinsed with 7 % nitric acid followed by reagent water.

Organic-free water was prepared by first exposing it to high intensity UV radiation for 30 min. Next, the water was heated to boiling and then cooled by purging with high purity nitrogen. Water prepared in this manner was stored in a clean, air-tight glass container.

Method detection limits using this technique are given in Tables B.2 and B.3.

Table B.2: **Method detection limits for sampling sessions 1 & 2 analyzed May through July, 1986.**

	ng/l				
	benzene	toluene	p-xylene	m-xylene	o-xylene
#1	39.62	88.82	54.29	82.38	83.06
#2	29.70	72.70	40.65	83.32	85.80
#3	30.60	61.30	39.22	68.48	95.29
#4	80.10	100.32	62.60	95.62	98.86
#5	58.76	101.34	53.34	91.76	89.32
#6	50.66	91.54	41.60	81.32	91.26
#7	44.44	97.80	48.89	90.40	89.94
#8	48.14	98.46	51.62	85.44	87.12
#9	95.65	97.90	60.92	91.10	97.88
#10	53.32	95.46	34.62	74.64	78.74
#11	73.36	94.52	79.44	83.58	82.42
#12	55.30	101.10	44.10	81.92	96.24
X	54.97	91.77	50.95	84.18	89.66
Xc	85.74	86.52	83.22	86.58	88.50
S	20.00	12.40	12.45	7.55	6.51
S%	36.38	13.52	24.44	8.97	7.26
E%	-36.05	6.07	-38.77	-2.77	1.31
MDL	62.86	38.99	39.14	23.75	20.46

X : mean of replicate determinations

Xc : true value

S : standard deviation

S% : relative standard deviation

E% : relative error

MDL : method detection limit (99 % confidence level)

Table B.3: Method detection limits for sampling sessions 3 & 4 analyzed August and September, 1986

	ng/l				
	benzene	toluene	p-xylene	m-xylene	o-xylene
#1	19.81	44.41	27.14	41.19	41.54
#2	14.85	36.35	20.34	41.65	42.90
#3	15.30	30.65	19.51	34.24	47.54
#4	40.05	50.16	31.30	47.81	49.43
#5	28.38	50.57	25.67	45.88	44.66
#6	25.33	45.77	20.80	40.66	45.63
#7	22.22	48.90	24.44	45.20	44.97
#8	23.07	49.23	25.61	42.72	43.58
#9	48.33	49.95	30.46	45.55	48.94
#10	26.66	47.73	17.41	37.42	39.37
#11	36.69	47.26	39.72	41.79	41.21
#12	29.15	50.55	23.05	40.96	48.12
X	27.49	45.89	25.45	42.09	44.83
Xo	44.37	43.26	41.51	43.29	44.25
S	10.00	6.20	6.23	3.78	3.25
S%	36.38	13.51	24.44	8.97	7.25
E%	-38.05	6.07	-38.77	-2.77	1.31
MDL	31.43	19.49	19.57	11.87	10.23

X : mean of replicate determinations

Xo : true value

S : standard deviation

S% : relative standard deviation

E% : relative error

MDL : method detection limit (99 % confidence level)

B.3 Chloride

Neither field or laboratory samples for chloride analysis required preservation. Chloride samples were analyzed using the automated wet chemical procedure described by Patrick et al. (1985) with detection limits of about 1 mg/L. This method requires a sample volume of about 1 ml.

B.4 Nitrate

Samples collected in the field were immediately acidified to preserve the nitrate during storage prior to analyses. Samples from laboratory experiments were not preserved since they were analyzed immediately. Acidified nitrate samples were neutralized immediately prior to analysis using ammonium hydroxide solution. All nitrate samples were analyzed using the automated cadmium reduction method (Franson, 1985). This method can be used to determine total nitrate plus nitrite, or, by a second subsequent analysis, nitrite singly. Due to time constraints and the large number of samples from the field, it was decided to analyze for nitrite plus nitrate with occaisional double analyses for nitrite singly. Nitrite concentrations were found to be well below 1.0 mg/L, therefore it was assumed that the single analyses were essentially measuring nitrate. laboratory samples were occaisionally analyzed for both nitrate and nitrite. The detection limit using this method is 0.06 mg/L N as NO_3^-.

B.5 Dissolved Oxygen

Dissolved oxygen measurements were made on water samples volumes varying from 18 to 50 ml. Procedures for collection of these samples vary according to the experiment and are discussed elsewhere. Samples were collected in glass syringes or sealed hypovials. All measurements were made using the Winkler technique with azide modification.

The technique consists of adding 0.1 cm^3 of each of manganese sulphate solution and alkali-iodide-azide solution per 10 cm^3 of water sample. The methods for preparation of all reagants and titrating solutions are given in detail by APHA et al. (1985). Reagants are added to samples in syringes by removing the needle tip and adding solutions via syringe through the neck of the sample syringe. A positive pressure is maintained on the plunger to reduce chances of contamination by atmospheric oxygen. If the sample is contained in a sealed hypovial, a small diameter needle tip was inserted through the samples's septa while the reagants were added via a 1 cm^3 plastic syringe. This extra needle tip allowed excess sample water to overflow during addition of the reagants thereby maintaining a constant volume. The sample was then shaken 20 times and the flocculent was allowed to settle. 0.1 cm^3 of phosphoric acid was added per 10 cm^3 of sample in the same manner used for addition of the first two reagants. The acidified sample was then transferred to an erlenmeyer flask and titrated using a standardized 0.0025 N potassium dichromate solution or a 0.00025 N solution if the sample volume was 5 ml. The method for standardization is given by APHA et al. (1985). Starch was added as an endpoint indicator. Detection limits for this method are 0.2 to 0.6 mg/L.

B.6 Nitrous Oxide

Water and gaseous samples from laboratory experiments were analyzed for nitrous oxide using gas chromatography. 20 cm^3 water samples were collected in glass syringes. These samples were prepared by adding 10 cm^3 of purified helium to the sample in the syringe. The sample and helium were allowed to equillibrate at 24^0C for 4 hours. Gas samples did not require this initial preparation. A 4 cm^3 aliquot of the gas phase was injected onto a Porapak Q (100/120 mesh) 6' x 1/8" stainless steel column and analyzed isothermally using a thermal conductivity detector. The total mass of nitrous oxide in the gas phase and dissolved in water was determined using the method described by Moraghan and Buresh (1977). The method detection limit for nitrous oxide using this method is approximately 0.5 mg/L.

B.7 Biodegradation Products

Organic acids or biodegradation products were qualitatively analyzed for using the method detailed by the USEPA (1982b). One litre water samples were serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2. The methylene chloride from the acid extraction was concentrated to a volume of 1 cm^3 and analyzed using a Hewlett-Packard gas chromatograph (model 5890) coupled with a Hewlett-Packard mass selective detector (model 5970).

B.8 Aerobic Plate Count

Estimation of the number of viable aerobic bacteria in aquifer material was made as follows. 10 g of aquifer material were shaken vigorously with 90 mls of .85% (w/v) sterile saline solution for 5 minutes. 10 cm^3 of the suspension were serially diluted to 5 different concentrations and 0.1 cm^3 aliquots of each dilution were pipetted onto soil extract agar (SEA) or R2A spread plates. Each dilution was plated in quintuple. The plates were incubated at 25^0C for 7-14 days. Colonies that grew on the plates were counted using a colony counter.

Soil extract agar contained, per litre, 900 cm^3 distilled water, 100 ml soil extract, 0.5 g yeast extract, 0.01 g ferric phosphate, 2.5 g glucose and 15 g agar at a pH of 6.8. Soil extract was made by autoclaving 1 kg of top soil in 2 L of distilled water. After cooling, the liquid extract was clarified by centrifugation and filtration.

R2A medium used on spread plates contained 0.5 g yeast extract, 0.5 g proteose pepton, 0.5 g casamino acids, 0.5 g glucose, 0.5 g soluble starch, 0.3 g K_2HPO_4, 0.05 g $MgSO_4.7H_2O$, 0.3 g sodium pyruvate and 15 g agar in 1 litre of distilled water (Reasoner and Geldreich, 1985). The pH was adjusted to 7.2.

B.9 Radioactive Methods

^{14}C radioactivity in laboratory microcosms associated with benzene, carbon dioxide and as intermediate biodegradation products dissolved in the water was quantified in the following manner. The microcosms were first made alkaline by the injection of 0.30 cm^3 of 5N NaOH to convert carbon dioxide to the carbonated form so it was not stripped from the groundwater during purging. The microcosm was then shaken for 5 min at 3000 rpm followed by centrifugation at 3000 rpm for 10 minutes to remove the suspended particulates. Total radioactivity in the water was determined by removing 2 cm^3 of the groundwater to a scintillation vial in which 3 cm^3 of aqueous liquid scintillation cocktail (Beckman Ready-Solv MP, Beckman Instruments, Canada) was added.

Total radioactitivity associated with benzene was determined by hexane extraction. 2 cm^3 of hexane, containing the internal standard m-fluorotoluene, was injected into the microcosm. The microcosm was shaken at 3000 rpm for 15 min and then placed in the centrifuge and spun at 3000 rpm for 10 min,. After the two phases separated, 0.5 cm^3 of the hexane phase was transfered to a scintillation vial to which 5 cm^3 of Beckman NA scintillation cocktail for non-aqueous samples was added. A further 0.20 cm^3 of the hexane phase was transferred from the microcosm to a Reacti-ial (Pierce Chemical Co., Il) and was analyzed by GC (section B.1) to confirm the presence of benzene. The mininert valve was then removed from the microcosm and the remaining hexane was taken off by syringe and a crimp cap with a teflon liner was installed. The microcosm was then purged with nitrogen gas for 30 min at 50 cm^3/min to remove the remaining benzene and hexane. After purging, 2 cm^3 of the remaining groundwater was removed to a scintillation vial to which 3 cm^3 of aqueous liquid scintillation cocktail (Beckman Ready-solv MNP, Beckman Instruments, Canada) had been added.

To quantify $^{14}O_2$, two scintillation vials containing 17 cm^3 of a CO_2 absorbing scintillation cocktail were connected in line with the microcosm. This cocktail was a mixture of CO_2 absorber (Carbo-Sorb, Packard Instrument Co., Il) and a scintillation cocktail (Permaflour-V, Packard Instruments, Il) in a ratio of 53% Carbo-Sorb balanced with Permafluour-V (Qureshi et al., 1985) stored under nitrogen. 0.4 cm^3 of concentrated H_2SO_4 was injected into the microcosm which was purged at a flow rate of 50 cm^3/min for 10 min. Finally 2 cm^3 of the remaining groundwater was removed to a scintillation vial to which 3 cm^3 of the Beckman Ready-Solv MP aqueous liquid scintillation cocktail had been added. The radioactivity remaining was due to the presence of water-soluble organic breakdown products of benzene that were not stripped from the water at any pH. Measurement of the radioactivity in the scintillation cocktails was performed on a MARK III Liquid Scintillation Spectromemter. The raw counts were corrected for background, quenching and dilution factors.

B.10 References

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Appendix C

DETECTED BTX CONCENTRATIONS

Piezometer	Concentrations (ng/L)				
	Benzene	Toluene	p-Xylene	m-Xylene	o-Xylene
9 September, 1985					
29,3-12	3400				
29,4-14	116000				
30-4-13	2700				
30,4-14	2100				
31,5-13	4600				
32,5-12	21000				
32,5-13	3100				
26 September, 1985					
29,4-14	135000				
32,5-13	5600				
33,5-12	6500				
3 October, 1985					
29,4-14	8200				
29,4-15	2500				
9 October, 1985					
30,4-15	2600				
27 May, 1986					
		all below 2000 ng/L			
5 June, 1986					
		all data lost			
11 June, 1986					

44,0-9	5 (5)	146 (128)	20 (20)	50 (48)	20 (20)
-11	102 (41)	278 (256)	6 (7)	40 (30)	23 (23)
-13	31 (30)	91 (91)	0 (0)	44 (44)	13 (13)
-14	76 (15)	78 (64)	0 (0)	30 (29)	38 (8)
44,4-9	45 (44)	295 (295)	23 (23)	123 (123)	55 (55)
-11	0	197 (179)	113 (113)	137 (135)	65 (65)
-13	0	196 (178)	4 (4)	34 (32)	40 (40)
-14	6 (5)	194 (194)	9 (9)	53 (53)	22 (22)
44,8-9	41 (40)	181 (181)	19 (19)	106 (106)	43 (43)
-11	6 (6)	113 (113)	3 (3)	73 (73)	28 (28)
-13	8 (7)	206 (206)	10 (10)	95 (95)	42 (42)
-14	131 (70)	352 (338)	21 (21)	115 (114)	53 (53)
44,12-9	108 (47)	260 (246)(	45 (45)	168 (167)	83 (83)
-11	81 (21)	147 (133)	16 (16)	110 (109)	60 (60)
-13	14 (13)	155 (155)	29 (29)	120 (120)	47 (47)
-14	92 (91)	217 (217)	119 (119)	141 (141)	73 (73)

Bracketed values have been corrected for blanks.

9 July, 1986

44,0-4	-	24*	11*	44	17*
-6	-	102	15*	46	19*
-8	-	74	18*	48	16*
-10	-	45	-	22	3.5*
-12	-	-	-	-	-
	-				
-14	-	135	-	24	3.1*
44,4-4	-	74	-	30	10
-6	-	220	24*	7.6*	
-8	-	-	-	24	4.8*
-10	-	53	38*	7.6*	
-12	-	6.6*	-	11*	-
-14	-	13*	-	6.6*	-
44,8-4		Lost			
-6	-	24*	-	37	1.2*
-8	-	7.6*	-	31	3.5*
-10	-	-	-	4.0*	3.5*
-12	-	4.6*	-	15*	-
-14	-	325	-	1.1*	-
44,12-4	-	572	-	28	19*
-6	-	78	-	6.3*	-
-8	-	698	-	22	12*
-10	-	172	-	13*	14*
-12	-	346	-	6.0*	-
-12	-	346	-	6.0*	-
-14	-	115	-	5.2*	2.7*

34,25-12	-	17*	-	-	-
-14	-	-	-	-	-
24 July, 1986					
44,0 -4	-	151	23*	57	77
-6	16*	159	24*	74	75
-8	-	93	13*	55	67
-10	-	140	14*	53	41
-12	-	92	9.2*	47	61
44,4 -4	-				
-6	6.1*	114	11*	28	61
-8	-	56	8.7*	52	63
-10	-	65	35*	93	89
-12	7.8*	138	4.2*	20*	39
-14	-	166	6.0*	40	46
44,8 -4	2.6*	69	20*	55	111
-6	-	70	14*	55	80
-8	-	104	35*	75	74
-10	22*	82	17*	45	60
-12	-	128	16*	62	71
-14	-	92	-	22*	21
44,12-4	-	170	24*	60	95
-6	12*	157	15*	47	64
-8	1.1*	208	24*	72	93
-10	-	120	23*	61	57
-12	2060	1840	865	973	1460
-14	9.5*	478	9.4*	35	32
34,25-4	-	77	9.4*	45	74
-8	-	61	-	26	39
-12	-	58	-	12*	50
29 August, 1986					
34,25-6[1]	-	-	-	-	-
blank[2]	-	-	-	-	-
52,8-4	8.4*	15*	-	6.2*	-
-6	-	-	-	-	-
-8	-	-	11*	-	-
-10	-	-	-	-	-
-12	-	-	-	-	-
blank	-	-	-	-	-
52,4-4	-	-	58	-	-
-6	22*	75	20	15	40
-8	10*	52	7.4*	0.9*	42
-10	-	33	6.1*	-	-
-12	4.3*	36	8.8*	1.4*	-
blank	-	-	-	-	-
34,25-6	-	-	-	-	-
44,0-12	-	11*	-	3.7*	-

-14	-	-	-	1.3*	-
44,4-12	-	-	-	-	-
-14	-	-	-	-	-
blank	-	-	-	-	-
44,8-12	-	-	-	-	-
-14	-	0.3	-	-	-
44,12-12	-	-	-	-	-
-14	-	-	-	-	-
blank	-	-	-	-	-
34,25-6	-	-	-	-	-
blank	-	-	-	-	-

23 September, 1986

GC/MS malfunction - no data

- : not detected
* : below method detection limits: see Appendix B
1 : background groundwater
2 : organic free water sampled with the manifold :EAPP

Appendix D

EXPERIMENT 3 RESULTS

The distribution of ^{14}C activity and nitrate, nitrite and D.O. concentrations was found to be as follows:

	^{14}C activity (% Distribution)				NO_3^-	NO_2	O_2
Condition	Day	Benzene	CO_2	H_2O	(mg/l)		
Benzene + NO_3	4	90.29	0.52	9.19	154.22	2.02	
	7	85.23	4.80	9.66	124.00	1.91	
	33	81.76	11.88	6.36	21.21	25.34	
	47	86.17	9.39	4.43	0.00	0.00	
	61	81.55	15.69	2.77	962.84	13.89	
	99	83.52	15.47	1.01	312.62	36.68	
Benzene + O_2	4	89.68	2.37	7.96			0.59
	7	86.55	7.11	6.33			0.39
	33	80.55	13.88	5.57			0.39
	47	74.04	19.94	6.02			0.00
	61	57.38	36.20	6.43			0.00
	99	70.16	20.40	9.44			0.00
Benzene	4	86.11	3.00	10.89			
	7	80.11	1.40	18.49			
	33	75.16	15.40	9.44			
	47	78.38	13.61	8.01			
	61	70.73	22.30	6.97			
	99	21.79	27.09	51.12			
Benzene + NO_3 + Gasoline	4	87.53	1.87	10.60	130.38	0.47	
	7	82.79	2.90	14.31	129.01	1.38	
	33	82.52	11.51	5.97	29.69	28.43	
	47	83.99	6.87	9.15	0.00	0.00	
	61	79.30	16.64	4.07	968.09	8.65	
	99	65.07	33.05	1.88	178.03	24.16	
Benzene + O_2 + Gasoline	4	90.48	2.92	8.55			0.74
	7	83.57	7.88	6.60			0.16
	33	93.76	15.94	7.56			0.20
	47	74.64	19.11	6.26			0.00
	61	76.46	14.24	9.30			0.00
	91	40.52	41.33	18.15			0.00

Benzene + Gasoline	4	81.89	5.02	13.09			
	7	79.10	7.55	13.36			
	33	73.56	8.07	18.36			
	47	67.54	19.81	17.64			
	61	56.38	28.91	14.70			
	99	79.93	9.45	10.64			
Benzene + NO_3 Sterile	4	100.00	0.00	0.00	156.29	0.00	
	7	99.49	0.52	0.00	141.61	0.00	
	33	96.57	3.43	0.00	142.63	0.00	
	47	97.69	2.31	0.00	176.93	0.00	
	61	99.51	0.49	0.00	992.68	0.00	
	99	99.39	0.61	0.00	939.58	0.00	
NO_3^-	4				125.20	1.90	
	7				129.90	1.86	
	33				21.09	16.75	
	47				0.00	0.00	
	61				1047.04	13.89	
	99				155.08	31.14	
O_2	4						1.00
	7						0.39
	33						0.14
	47						0.00
	61						0.00
	99						0.00
No Addition (sterile)	4						0.00
	7						0.00
	33						0.00
	47						0.00
	61						0.00
	99						0.00